CRREL REPORT 92-5

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Waterfowl Mortality in Eagle River Flats, Alaska

The Role of Munitions Residues

Charles H. Racine, Marianne E. Walsh, Charles M. Collins, Darryl J. Calkins, Bill D. Roebuck and Leonard Reitsma

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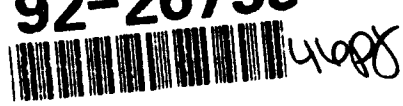

For conversion of SI metric units to U.S./British customary units of measurement consult ASTM Standard E380, Metric Practice Guide, *published by the American Society for Testing and Materials. 1916 Race St., Philadelphia, Pa. 19103.*

Cover: Eastern portion of Eagle River Flats, showing the Eagle River, Knik Arm and ponds where waterfowl feed.

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U.S. Army Corps of Engineers
Cold Regions Research & Engineering Laboratory

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PREFACE

This report was prepared by Charles H. Racine, Research Biologist, Geological Sciences Branch, Research Division; Marianne E. Walsh, Research Physical Scientist, Applied Research Branch, Experimental Engineering Division; Charles M. Collins, Research Physical Scientist, Alaska Projects Office; Darryl Calkins, Chief, Geological Sciences Branch, Research Division, U.S. Army Cold Regions Research and Engineering Laboratory; Bill D. Roebuck, Toxicologist, and Leonard Reitsma, Avian Ecologist, Dartmouth College.

Funding for this effort was provided by the U.S. Army Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, Maryland (Installation Restoration Division). Captain Steven Bird, Project Officer, provided valuable assistance.

The authors gratefully acknowledge many units within the U.S. Army 6th Infantry Division (Light) that provided support. They particularly thank William Gossweiler, Wildlife Biologist, Ft. Richardson DEH, for his valuable help with logistical arrangements, which included scheduling helicopter support, organizing supplies and helping with countless other tasks. The authors are indebted to the personnel of the 176th Ordnance Detachment (EOD) for escorting the sampling parties into Eagle River Flats.

The Eagle River Flats Interagency Task Force, composed of representatives from the U.S. Fish and Wildlife Service (Rodney Jackson, David McGillivary, William Eldridge), Alaska Dept. of Fish and Game (Dan Rosenberg), Alaska Dept. of Environmental Conservation and the U.S. Environmental Protection Agency (Douglas Johnson), offered valuable suggestions and helped with actual field work. Daniel Rosenberg and William Eldridge supplied waterfowl specimens from both ERF and Susitna Flats, and they offered valuable observations.

The Alaska District Corps of Engineers provided survey services and chemistry laboratory facilities; Clare Jaeger from the Alaska District was particularly helpful with the chemistry laboratory.

CRREL personnel provided considerable assistance: Captain Jeffrey Meyer interviewed Ft. Richardson range control personnel, helped in the field and contributed information on artillery practices and munitions. Dr. Thomas F. Jenkins offered technical advice concerning the chemistry of explosives and white phosphorus; Paul Miyares and Cora Farnsworth assisted in the analysis of water and sediment samples; Lawrence Gatto and Andrew Bruzewicz assisted with the GIS mapping; David Cate, Dr. Jenkins and Dr. Daniel Lawson reviewed and edited this report.

Several Dartmouth College students also participated in the study. Pamela Buchli, graduate student in toxicology, and Gregory Goldfarb, undergraduate biology major, assisted with the laboratory toxicity studies.

Dr. Randall Wentzel of the Chemical Research Development and Engineering Center provided us with valuable information on white phosphorus toxicity to waterfowl.

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ACRONYMS AND ABBREVIATIONS

AEHA	Army Environmental Hygiene Agency
AK Dist., COE	Alaska District, Corps of Engineers
2-Am-4,6-DNT	2-amino-4,6-dinitrotoluene
4-Am-2,6-DNT	4-amino-2,6-dinitrotoluene
CRL	certified reporting limit
CRREL	Cold Regions Research and Engineering Laboratory
DEH	Directorate of Engineering and Housing
DMD	distance measure device
DNB	1,3-dinitrobenzene
2,4-DNT	2,4-dinitrotoluene
2,6-DNT	2,6-dinitrotoluene
EOD	explosive ordnance disposal
EPA	Environmental Protection Agency
ERF	Eagle River Flats
ESE	Environmental Science and Engineering, Inc.
GC-FPD	gas chromatography-flame photometric detector
GCMS	gas chromatography-mass spectrometry
GI	gastrointestinal tract
GIS	geographic information system
GRASS	Geographical Resources Analysis Support System
HC	hexachloroethane-zinc mixture
HE	high explosive
HMX	octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
HPLC	high-performance liquid chromatography
ID	internal diameter
ILL	illumination
M1	a propellant composition
NB	nitrobenzene
NT	nitrotoluene (ortho, meta, and para isomers)
NWHRC	National Wildlife Health Research Center
ORP	oxidation–reduction potential
P_4	white or elemental phosphorus
PCBs	polychlorinated biphenyls
ppm	parts per million (mg/g or mg/L)
RDX	hexahydro-1,3,5-trinitro-1,3,5-triazine
THF	tetrahydrofuran
TNB	1,3,5-trinitrobenzene
TNT	2,4,6-trinitrotoluene
USATHAMA	U.S. Army Toxic and Hazardous Materials Agency
UTM	Universal Transverse Mercator
UV	ultraviolet
uxo	unexploded ordnance
WP	white or elemental phosphorus

Waterfowl Mortality in Eagle River Flats, Alaska
The Role of Munitions Residues

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DARRYL J. CALKINS, BILL D. ROEBUCK AND LEONARD REITSMA

INTRODUCTION

During the past ten years, hundreds of migrating ducks have been found dead during the fall and spring migrations in Eagle River Flats (ERF), an estuarine salt marsh in upper Cook Inlet on Fort Richardson (Fig. 1 and 2). The cause of this mortality has remained a mystery despite numerous attempts by federal and state agencies over the past five years to identify the causes. Analyses of duck carcasses from Eagle River Flats by wildlife laboratories ruled out avian diseases and lead poisoning, and numerous sediment and water samples failed to show significant levels of any toxic compound, including heavy metals. The 1000-ha salt marsh has been used as a U.S. Army artillery impact range into which artillery shells, mortars, rockets and illumination flares have been fired over the past 40 years (Fig. 3).

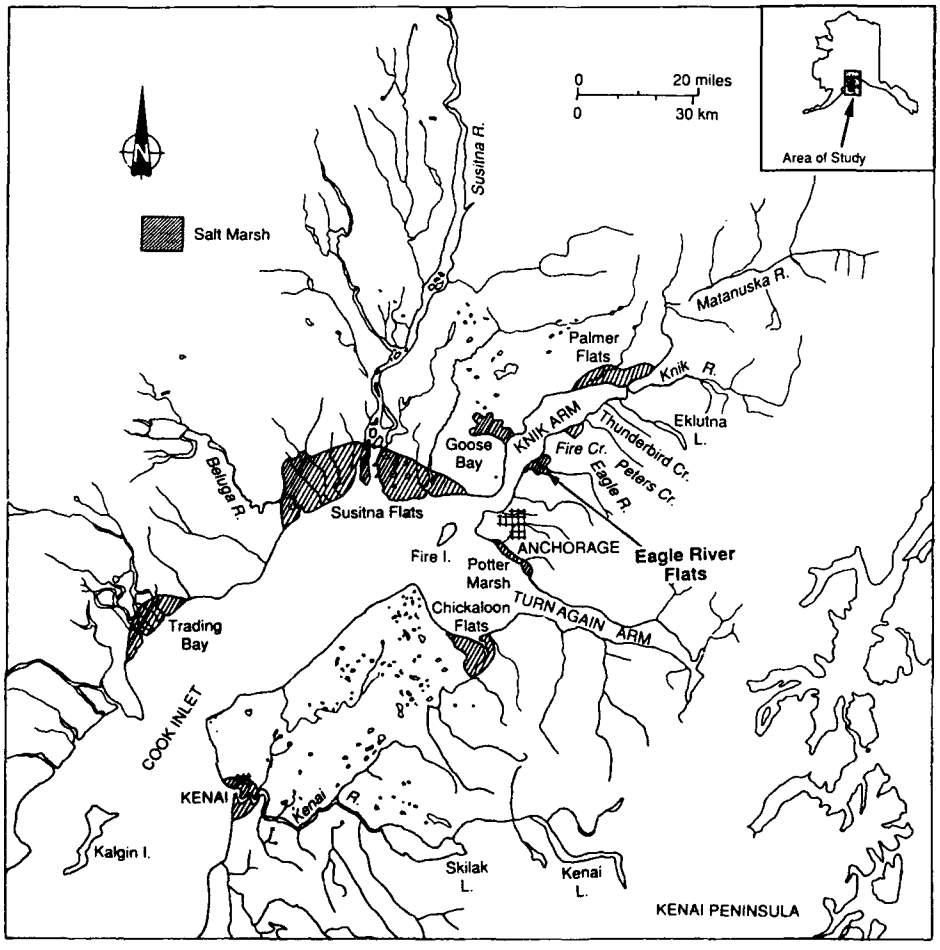


Figure 1. Upper Cook Inlet area, showing the location of Eagle River Flats (ERF) and several other estuarine salt marshes (shaded areas) mentioned in this report.

Figure 2. Eagle River Flats viewed over Knik Arm toward the east, with the Chugach Mountains and Ft. Richardson visible in the background. Note the ponds and flooded areas on either side of Eagle River.

Figure 3. Explosion craters in the salt marsh vegetation of Eagle River Flats. The Eagle River is visible in the background.

Because a study by USATHAMA (ESE 1989) concluded that munitions are the cause of waterfowl mortality in ERF, the Commanding General, 6th Infantry Division, (Light) closed ERF as an impact area in February 1990. Despite closure, large numbers of waterfowl continued to die during the 1990 spring and fall migrations.

Because of CRREL's expertise in chemical analyses for munition residues in soil and water and CRREL's expertise in Alaskan wetlands ecology, we were requested by USATHAMA to test the hypothesis that munition compounds are the cause of mortality in ERF. Our four major objectives during 1990 were to:

- Conduct chemical and physical analyses of sampled sediments, water and affected waterfowl tissue;
- Determine the field behavior of affected waterfowl in relation to feeding and death;
- Conduct controlled feeding experiments with suspected compounds; and
- Determine the basic environmental conditions in ERF and the military use of the area that could affect the types, location, storage or movement of munition compounds.

We based our approach to the problem on four basic conditions or assumptions:

- Incomplete combustion and subsequent storage of explosives may occur in the standing water and saturated soils of a wetland environment;
- Because certain species of dabbling ducks appear to be the principal victims, the poisons probably reside in sediments, which are processed by ducks when they submerge their heads in shallow ponds and mandibulate the bottom sediments in search of edible solids;
- Only a relatively small percentage of the ducks that enter and feed in ERF die; therefore, the distribution of the poison must be heterogeneous and sporadically distributed in certain areas of this 1000-ha marsh; and
- Because ducks have continued to die despite the cessation of firing in February 1990, the poison does not degrade rapidly in the salt marsh sediments.

These conditions required much more intensive sampling of sediments than was conducted by prior studies in order to locate or detect the presence of a poison. Because munitions residues have not been conclusively detected in the past, our initial objective was to determine if munitions residues do in fact occur anywhere in the sediments or water of ERF.

We also wished to investigate in more detail the feeding behavior of the affected duck species in ERF in order to determine where the ducks are feeding and what types of sediments are being processed by the ducks. The circumstances of mortality in terms of death rate, predation, onset of sickness and behavioral symptoms preceding death also needed to be understood for comparison with a controlled feeding experiment in the laboratory.

Our approach to the problem was to develop an understanding of the ERF salt marsh ecosystem in terms of vegetation, waterfowl, sediments and water relationships to provide basic environmental documentation for future studies of the problem. Then we wished to obtain as much information as possible on the types and amounts of munitions that have been used in ERF. We used evidence obtained at various stages of our field studies to modify and develop new hypotheses and suggest additional avenues of investigation.

BACKGROUND AND LITERATURE REVIEW

Waterfowl mortality

The mortality of waterfowl in ERF was first recognized in 1980, and investigations of the problem began in 1982. Tweten (1989) summarized studies conducted by the U.S. Fish and Wildlife Service, the Alaska Department of Fish and Game, the Army DEH and other agencies. Dabbling ducks, such as northern pintails, mallards and green-winged teal, and swans (trumpeter and tundra) are the most affected species. Mortality of dabbling ducks has been concentrated in four areas of ERF where suitable pond habitat is located (Fig. 4). These four areas have

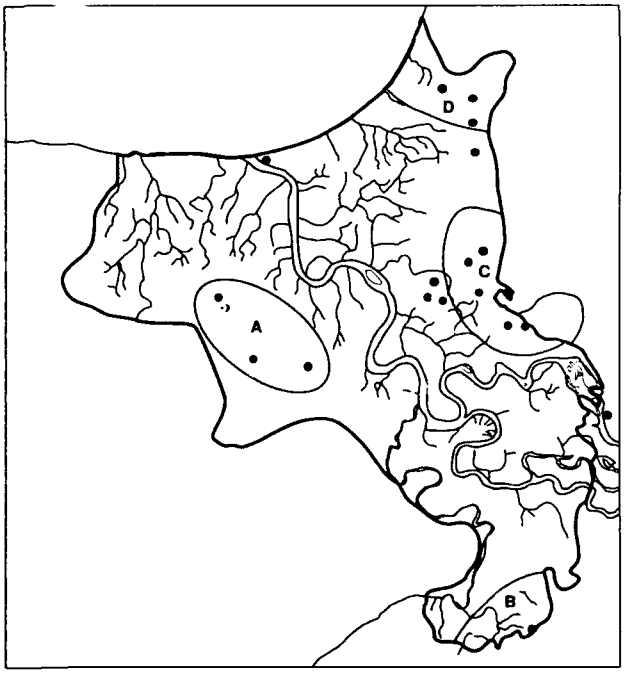


Figure 4. Approximate locations of water and sediment sample sites for a 1989 study by ESE. Also outlined are the four areas (A, B, C and D) where dabbling ducks congregate on ponds and where most of the mortality has been observed.

Table 1. Summary of waterfowl mortality counts made between 1982 and 1988.

Date	*Number of searches*	*Number of searchers*	*ERF area*	*Number of carcasses*
August 1982	1	1	Fox Point	n.d.*
September–October 1983	5	5	A	159
			B	21
			C	71
			D	117
Total				368
August 1984	4	2–11	A	140
September 1984	1	1	A	29
16 May 1985	1	8	C	70
20 April–7 October 1988	26	34	C, C/D	358†

* n.d. = not determined.

†† 573 feather piles also found.

Table 2. Numbers of carcasses and feather piles either observed or collected between 20 April and 7 October 1988 (Tweten 1989).

Species	*Fresh carcasses*	*Feather piles*
Northern pintail	117	118
Mallard	113	46
Green-winged teal	97	62
Northern shoveler	13	28
American wigeon	1	5
Gadwall	1	0
Least sandpiper	1	0
Semipalmated sandpiper	1	0
Dowitcher sp.	1	0
Yellowlegs	1	0
Swans	10	?
Bald eagle	1	0
Mew gull	1	0
Raven	0	1
Canada goose	0	2
Unknown ducks	0	254
Unknown shorebird	0	14
Unknown gull	0	1
TOTAL	358	573

been designated areas A, B, C and D by the various groups studying the problem.

Attempts to count and tabulate the numbers and species of bird carcasses in various parts of ERF were made between 1983 and 1990 (Tables 1 and 2). Accurate counts and estimates of waterfowl mortality in ERF are difficult, particularly from the air, because vegetation obscures the view and because eagles and other predators rapidly remove and consume the carcasses. We observed poisoned ducks hiding in tall vegetation, so that death often occurs in places difficult to observe. In early May eagles were seen to swoop down on duck flocks resting on the shallow ponds and capture individual birds that did not fly (presumably because they were dead or incapacitated). The eagles then flew to nearby drier ground or to a tree and devoured portions of the duck, leaving a pile of feathers and bones.

Many of the early mortality counts were made in conjunction with the collection of carcasses by the U.S. Fish and Wildlife Service for necropsy by the National Wildlife Health Research Center (NWHRC). Until 1989, mortality counts were made on foot and often involved five or more individuals walking over limited areas of the flats on a single day during either the spring or fall (Table 1). The most intensive count of dead birds involved 26 foot searches by 34 searchers in area C and part of D between 20 April and 7 October 1988. A total of 350 man-hours were spent on this count, and a total of almost 1000 dead waterfowl were tabulated. The distribution of species is shown in Table 2.

During the present study between mid-April and mid-October 1990, the Ft. Richardson wildlife biologist (William Gossweiler) made occasional counts of featherpiles and carcasses from an Army helicopter and also made notes on carcasses observed from the shore of area C ponds. A helicopter survey on 11 May revealed 17 duck feather piles on the ground between areas C and D. From opposite area C, seven duck carcasses (mainly teal) were observed floating in the ponds on 16 May. Helicopter surveys in June and July revealed no or only a few carcasses. However, by 31 July, six duck carcasses and two featherpiles were observed in ERF during an aerial survey. On 8–9 August two dead teal and four mallard carcasses were observed in area C from shore. On 16 August a total of 111 carcasses (mostly mallards teal and wigeon) were counted from a helicopter mortality survey. On 10 September a total of seven duck carcasses were sighted from the air.

Between late September and late October 1990, swan carcasses were sighted: six on 24 September, two on 28

Table 3. Summary of previous sediment and water analyses in Eagle River Flats.

Agency	*Date collected*	*Number of samples and location*	*Analyses*	*Results*
Sediment				
Army Environmental Hygiene Agency	6/85	7 from ERF; 2 from Goose Bay	Pesticides PCBs Explosives Metals	Negative Negative Negative Within background
Alaska Dept. of Environmental Conservation	9/88	3 from ERF	Semivolatiles Mercury Lead	Organics common to sediments Negative 16–22 mg/kg
Environmental Science and Engineering, Inc.	1989	26 from ERF; 1 from Cottonwood Slough	Volatiles; semivolatiles and explosives Inorganics	No major contamination from organic compounds Elevated concentrations of some inorganics
Water				
Army Environmental Hygiene Agency	6/85	7 from ERF; 2 from Goose Bay	Pesticides PCBs Explosives Metals	Negative Negative Negative Within background
Environmental Protection Agency, Corvallis, OR	7/88	3 from EOD Pond, Beaver Pond, and OP Vital Pond	Organochlorine Organophosphate pesticides	No definitive results
Alaska Dept. of Environmental Conservation	9/88	3 from ERF	Semivolatiles Mercury Lead	Diethyl phthalate (26 mg/L) Negative Negative
Environmental Science and Engineering, Inc.	1989	26 from ERF; 1 from Cottonwood Slough	Volatiles; semivolatiles and explosives Inorganics	No major contamination from organic compounds Elevated concentrations of some inorganics

September, 18 on 5 October, five on 9 October. Estimates of the 1990 swan mortality were set at around 40, compared with 9 or 10 in 1988 and 1989. Because of the size and conspicuous white plumage of swans, these counts are considered much more accurate than those of ducks.

Sediment and water samples

Sediment and water samples from ERF have been analyzed by the Army Environmental Hygiene Agency (AEHA), the Alaska Department of Environmental Conservation, the Environmental Protection Agency (EPA) and Environmental Science and Engineering, Inc. (ESE) (Table 3). No evidence of major contamination from explosives, pesticides, PCBs or other organic compounds was found. Mercury and lead were both considered at background concentrations. ESE did report finding aluminum, antimony, arsenic, barium, chromium, copper, iron, magnesium, manganese, nickel, phosphate, sodium and zinc at concentrations they considered elevated for Alaska but not high enough to cause the waterfowl mortality. Additional samples from ERF and three control areas, obtained during 1990, were analyzed by ESE for inorganic compounds. Except for the 1989 ESE study (Fig. 4), it is difficult or impossible to determine the general locations in ERF where samples were obtained.

Waterfowl tissue

In an attempt to determine the cause of the waterfowl mortality, 80 bird carcasses collected from ERF between 1983 and 1988 were examined at the U.S. Fish and

Wildlife Service National Wildlife Health Research Center (AFWRC and NWHRC 1988). Gross necropsy and histopathological examinations gave no evidence for trauma or for bacterial, viral or parasitic disease. Tests for cholinesterase inhibition were negative, as were tests for lead, mercury, zinc, magnesium or arsenic poisoning. In 1983 the gastrointestinal (GI) tracts from four birds were analyzed for total phosphorus, and the concentrations found were considered to be abnormally high (1730–8500 ppm dry wt). In 1984, additional analyses for total phosphorus were performed on the GI tracts from four birds collected at ERF and four control birds (the report does not indicate where these birds came from). The concentrations in the four birds from ERF ranged from 920 to 1190 ppm wet weight, compared to 750–900 ppm wet weight for the controls. At the time the lab did not consider there to be a significant difference between the two groups. However, in a draft proposal submitted in 1988 by NWHRC, "further investigation of phosphorus as a potential toxicant" was considered necessary (AFWRC and NWHRC 1988).

Fifteen specimens were sent in 1988 to the Patuxent National Wildlife Research Center and analyzed at the University of Missouri Environmental Trace Substances Research Center. Kidney and liver tissues from five mallards, five northern shovelers, one pintail, two greenwing teal, one trumpeter swan and one bald eagle were analyzed for 14 trace elements (aluminum, arsenic, beryllium, cadmium, chromium, copper, iron, lead, manganese, mercury, nickel, selenium, thallium and zinc). The concentrations of these elements in the waterfowl tissue were less than those associated with acute or chronic mortality.

ESE also analyzed waterfowl tissue for metals (aluminum, antimony, arsenic, barium, beryllium, cadmium, calcium, chromium, cobalt, copper, iron, lead, manganese, molybdenum, nickel, selenium, thallium, vanadium and zinc). Concentrations of these metals in the livers from four wild ducks from ERF were compared with the concentrations found in the livers from three wild ducks from Cottonwood Slough. In addition, liver tissue was analyzed from ducks used for a caged bird study (14 birds from ERF and 2 birds from Cottonwood Slough). No abnormal concentrations were found. Gross necropsy and histopathological examinations gave no indication of infectious disease. ESE planned to analyze for explosives, but they concluded that a suitable analytical method was not available.

ENVIRONMENTAL SETTING

Eagle River Flats at the mouth of the Eagle River (Fig. 1) is an estuarine salt marsh on the south side of Knik Arm in upper Cook Inlet. Other salt marshes on Knik Arm include Fire Creek just north of ERF, Goose Bay and Palmer Flats. Susitna Flats near the lower end of Knik Arm is one of the largest intertidal salt marsh areas in Cook Inlet. Estuarine areas in Cook Inlet have wide outflow areas that narrow gradually inland. Averaging 2.75 km in width near the coast, ERF is bounded inland by a sharp topographic and vegetation boundary of spruce- and birch-covered uplands (Fig. 2). Vegetated mudflats, sedge marsh and open water ponds are arranged in zones running parallel to the main river channel and its distributaries (Fig. 2).

Most of upper Cook Inlet dropped 0.3–1.2 m during the 1964 earthquake (Ovenshine et al. 1976). The shoreline of Knik Arm in the vicinity of ERF dropped 0.6 m (Small and Warton 1969). However, because of the massive quantities of silt and clay carried by major rivers entering Cook Inlet, many of these marshes in Cook Inlet have aggraded to pre-earthquake levels (Ovenshine et al. 1976).

The drainage area of the Eagle River basin is approximately 192 mi^2 (497 km^2). Glaciers cover 13% of the basin. The flow rate of Eagle River was gauged from October 1965 to June 1981. Based on this record the average discharge of the river is 519 ft^3/s (14.7 m^3/s). The maximum average discharge occurs in July and August and is associated with maximum glacial melt in the headwaters. The average July and August discharges are greater than 1500 ft^3/s (42.5 m^3/s), with peak discharges averaging greater than 2300 and 2700 ft^3/s (65.1 and 76.4 m^3/s), respectively. Occasional peak discharges greater than 3700 ft^3/s (105 m^3/s) occur, usually associated with a rainfall event in addition to glacial runoff.

Cook Inlet coastal salt marshes provide important feeding habitat for migrating waterfowl during the spring and fall (Lensink and Derksen 1986). Rosenberg (1986) showed that Cook Inlet tidal marshes were used most extensively by geese and dabbling ducks, particularly northern pintails and green-winged teal. It was the only habitat in which (migrant) tundra swans, brant, lesser snow geese and white-fronted geese were observed. Salt marsh habitat for migratory waterfowl is of limited extent in Alaska; Hall (1988), as part of the National Wetland Inventory, showed that while Alaska contained about the same acreage of estuarine habitat as the coterminous U.S. (21 million acres), a much smaller percentage (1.7%) of this is estuarine intertidal vegetated wetlands (salt marsh) than in the coterminous U.S. (22.2%).

Waterfowl use

The U.S. Fish and Wildlife Service (USFWS) has conducted seasonal aerial waterfowl surveys of ERF from 1988 through 1990 to support the various mortality studies. This information helps answer the question of

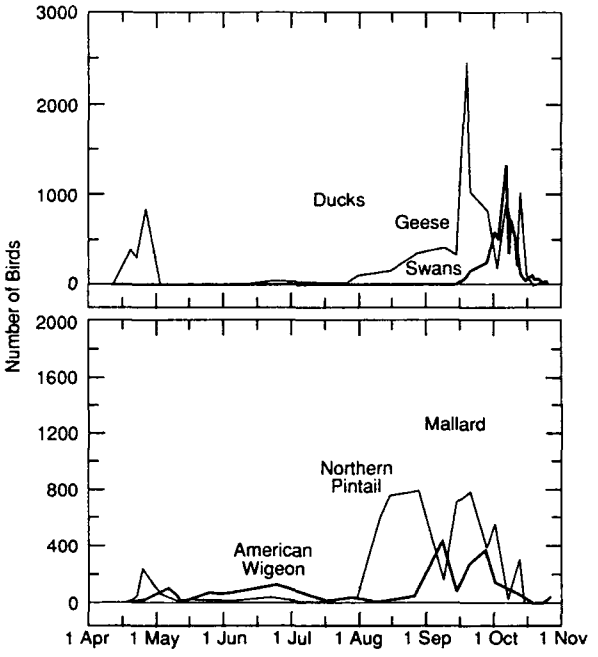


Figure 5. Waterfowl aerial census data for Eagle River Flats for April through November 1990 from a report by W. Eldridge (U.S. Fish and Wildlife Service, Anchorage).

how many and what species of birds utilize ERF and could potentially be exposed to the poison. William Eldridge (USFWS, Anchorage) described the results of the 1990 census and compared these results with those from 1988 and 1989. Figure 5, which is taken from his report, shows that waterfowl use is mainly limited to the two migration periods: spring (late April to early June) and fall (mid-August to mid-October). In most years waterfowl use is greater during the fall than during the spring. Daily and annual fluctuations in the numbers of birds using ERF are significant, making accurate estimates of numbers difficult. Without marking birds it is impossible to determine how many individuals remain on ERF from day to day or how many are replaced. One aerial survey on 3 October 1990 showed a total of 1345 swans and 1435 ducks distributed in the shallow ponds in ERF. Over 1000 Canada geese were also counted on the mud flats nearer Eagle River. Five days later another survey showed a raft of almost 1100 dabbling ducks (predominantly mallards). At this time an estimated total of 269 swans, 1860 ducks and 240 geese were also present. A small population of ducks, cranes and shorebirds remains and may breed in ERF throughout the summer. There is also variation in the numbers and species using each of the four habitat areas; swans were observed mainly in area D, while geese are most abundant in A. Ducks appear to be fairly evenly distributed among the four areas.

Tidal inundation

Cook Inlet and Knik Arm salt marshes are subject to large semidiurnal tidal fluctuations of 30–35 ft (9.1–11 m) (Fig. 6). Tidal inundation of the Eagle River Flats involves both the rise in the tide in Knik Arm (Cook Inlet) and overflow from the Eagle River as it meets the rising tide. A high tide of 32.4 ft (9.87 m) on 25 May 1990 covered the entire flats before receding. The highest 1990 annual tide was 33.2 ft (10.1 m) above mean low water on 29 March.

Due to the large discharge of Eagle River and its large size in relation to the flats, ERF may flood more frequently than other Cook Inlet estuaries, where flooding depends mainly on the tide. In the nearby Susitna Flats, Snow and Vince (1984) described only 15 flooding tides per summer in the outer mudflats, 11 for the inner mudflats, 3 for the outer sedge marsh and 2 for the inner sedge marsh.

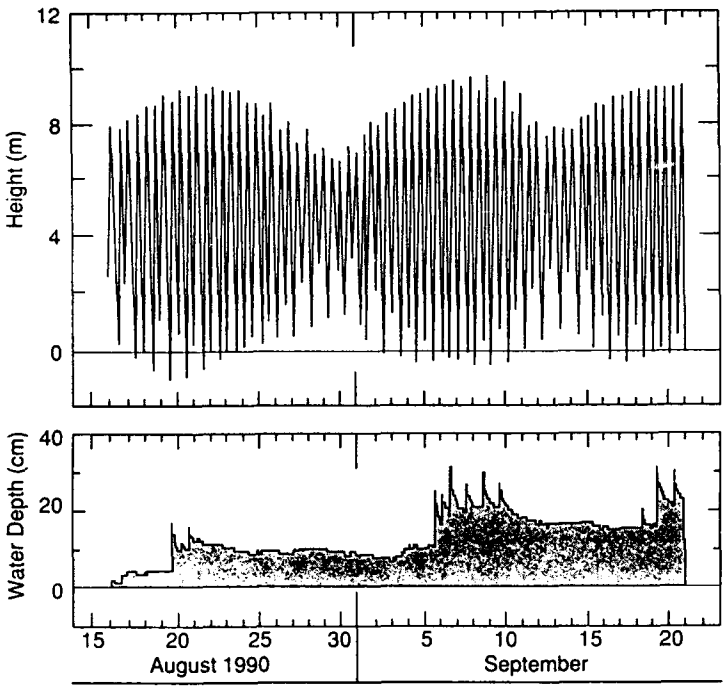
Between 16 August and 21 September 1990, the water depth in an area C pond was recorded hourly with a Druck pressure transducer attached to an Omnidata datalogger (Fig. 6). These measurements showed 11 flood events between 16 August and 21 September, or whenever the Anchorage tide tables reported tides greater than about 30 ft (9.1 m). However, this flooding was by fresh water from the Eagle River rather than salt water from Knik Arm. Tides of this magnitude [over 30 ft (9.1 m)] occur during at least five days in May, four in June, three in July, four in August and 11 in September. The magnitude of the inundation of ERF depends on the Eagle River discharge, the height of the tide and the wind direction.

Siltation

All of the major rivers flowing into Knik Arm are heavily loaded with fine glacially derived suspended sediment, so great quantities of silt are deposited in the tidal flats during the summer. Each time ERF is inundated, silts and clays are deposited. No direct measurements of deposition were obtained; however, rates determined elsewhere in upper Cook Inlet (Vince and Snow 1984) show rates of 5–12 mm per year on the mudflats. Because of the heavy silt load in Eagle River and the greater frequency of flooding, deposition may be higher in ERF than in other nearby salt marshes.

Soils

Hydrometer analyses of 15 sediment samples from ERF collected during the spring of 1990 showed that the silt content varied from 52 to 85%, while sand was consistently less than 3%. There was also variation in the particle size distribution between two areas; the clay fraction was only 13–27% in area A, compared with 30–47% in area C. Area C is closer to the Eagle River and may receive more of the fine "glacial flour" or clay



a. Levels from 1990 Anchorage tide tables from 16 August to 21 September.

b. Measured changes in water depth in a permanent pond next to the EOD in Eagle River Flats salt marsh during the same period.

Figure 6. Daily high and low tides.

particles from the river. Vince and Snow (1984) reported that the soil texture at a variety of salt marsh sites in nearby Susitna Flats averaged 34% sand and 38% silt, significantly higher sand levels and lower silt concentrations than in ERF. Measurements of pH in 36 water and sediment samples from ERF ranged from 7 to 8, or slightly alkaline.

The oxidation state of the sediments (App. A) influences the storage and fate of chemicals in salt marsh soils. Measured redox potentials of 131 sediment samples collected during August 1990 showed highly reduced sediments (less than –200 mV) in 44 of these samples. In 48 samples the redox potential ranged from –100 to –200 mV, and 38 samples ranged from –100 to 0 mV. Only one sediment sample had a positive redox potential.

Climate

The Anchorage area is in the transitional climate zone, between the extremes of the continental and maritime zones in Alaska. The Alaska Range north and northwest of Anchorage provides a barrier to the influx of very cold air from interior Alaska. To the northwest and southwest, Anchorage is bounded by the waters of Cook Inlet and Turnagain and Knik Arms, which provide a moderating influence on the climate. The average daily maximum temperature at Anchorage airport is 42.4°F (6.1°C), the average daily minimum temperature is 28.2°F (–2.2°C) and the annual mean is 35.3°F (1.9°C). The highest and lowest recorded temperatures are 86°F (30°C) and –34°F (–37°C) (NOAA 1989). The Anchorage bowl receives from 13 to 20 in. (330–508 mm) of precipitation annually, with the heaviest precipitation in July and August, when the winds are often from the southwest. Air masses move in from the Gulf of Alaska (southwest) and begin to rise over the Chugach Range behind Anchorage. This produces relatively heavy rainfall along the mountains and can contribute to high runoff events in the rivers draining the Chugach Range, including Eagle River.

Vegetation

Salt marshes contain vegetation zones related to gradients in elevation and the resulting differences in frequency and depth of flooding, salinity, drainage and rates and depths of sediment deposition. The general pattern and zones recognized by several studies in Cook Inlet are the same and generally include outer and inner mudflats, outer and inner marshes and shallow ponds (Snow and Vince 1984, Rosenberg 1986, Hanson 1951). In ERF these are arranged back from the coast of Knik Arm or away from the edge of Eagle River, and the salinity and the frequency of flooding presumably decrease along this gradient.

The outer mudflat zone nearest Knik Arm is bare or sparsely vegetated by alkali grass (*Puccinellia* sp.) or occasional annual species such as *Salicornia europea* or *Atriplex alaskensis*. Salinities in this zone are the highest, ranging from 15 to 25 ppt.

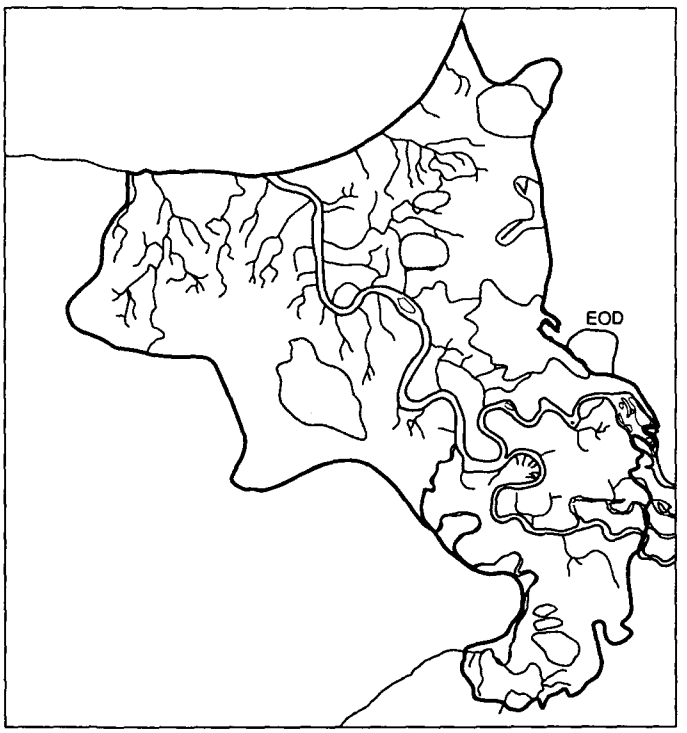


Figure 7. Distribution of ponds and areas where dabbling ducks concentrate during the spring and fall migrations.

Raised levees along the banks of Eagle River and the larger distributaries are among the best-drained habitats in the marsh. These are occupied by *Elymus* sp.

The inner mudflat zone is better vegetated than the outer mudflats and includes alkali grass and annual herbs in addition to *Triglochin maritimum* and *Plantago maritima*. Salinities of standing water in this zone range from 12 to 20 ppt. Geese frequently graze in this zone.

The outer sedge marsh consists of *Carex ramenskii*, *Triglochin maritima* and *Potentilla egedii*. Salinities in pools of this zone are 10–12 ppt.

The inner sedge marsh is dominated by the sedge *Carex Lyngbyaei*. Stands of this marsh are well developed in ERF (Hanson 1951) and are frequently over 1 m in height. The roots of this sedge form a dense tight mat that traps sediments and is up to 30 cm deep. New shoots of lyngby's sedge are produced in the fall and are consumed by migrating waterfowl. Salinities in this zone are 2–9 ppt.

Pools and ponds up to 50 cm deep occur in the inner marsh (Fig. 7). These ponds have interspersed clumps and islands of taller vegetation, emergent sedges and the bulrush *Scirpus validus*, which produces brown standing dead vegetation. *Hippurus tetraphylla* is common in shallower water from 10 to 30 cm deep. A rich aquatic vegetation develops in these ponds by late August, including *Potamogeton pectinatus*, *P. vaginatus*, *Ruppia spiralis* and *Zannichellia palustris*. Dying ducks were frequently found entangled in this vegetation. The salinity of the water in these ponds is between 2 and 9 ppt.

A shrub bog develops along the edge of ERF, particularly in the two embayment areas in the northeast and western edge of the flats. Species include *Myrica gale*, *Carex pluriflora*, *Calamagrostis canadensis*, *Potentilla palustris* and *Lathyrus palustris*. Salinity is less than 2 ppt in these shrub bog areas, and this area is essentially a fresh water wetland. Both cranes and swans were frequently observed in these areas.

Bird habitat

The ponds and pools described above are the major areas where dabbling ducks congregate to feed during the spring and fall migrations (Fig. 7). These are areas that flood at higher tides but are more or less permanent and vary in depth from 5 to 50 cm. In addition the coastline along Knik Arm and Eagle River itself are important.

Because ponds are the habitat used for feeding and resting by the dabbling ducks, the majority of dead ducks have been found in four areas of ERF where ponds and pools are most extensive (Fig. 4). These four areas have been designated areas A, B, C and D by the various groups studying the problem of waterfowl mortality in ERF.

Area A is on the west side of Eagle River in an area of shallow ponds and vegetated mudflats, with the open water areas interspersed with islands and stands of taller sedge and rush vegetation. A drainage slough to Eagle River divides the area.

Area B is at the south end of ERF where a fresh water stream (Otter Creek) meanders across the flats. Most of the vegetation consists of sedge marsh, and the relatively low elevations here result in salinities of 8–15 ppt.

Area C is on the east side of Eagle River along the upland edge of the salt marsh, which includes an explosive ordnance disposal area and several small fresh water inlets. A permanent pond of relatively deep water (up to 50 cm) occurs along the shoreline and grades into shallower ponds and mudflats toward Eagle River to the west. A well-developed inner sedge marsh marks the southern edge of this deeper pond.

Area D is in the northeast corner of ERF, where ponds are dotted with clumps and islands of sedges and rushes and where there is an embayment of shrub–bog vegetation. Swans frequent this area during the fall migration.

MUNITIONS USE IN EAGLE RIVER FLATS

Because this study tests the hypothesis that munitions are the primary cause of waterfowl mortality in ERF, this section summarizes what is known about the use of munitions in the Eagle River Flats impact area. The types of munitions, amounts used, chemical composition and toxicity are briefly described.

ERF has been used as an impact area for artillery training for approximately 40 years. Firing into ERF occurs from over 25 firing points up to 10 km from ERF. Targets consisting of derelict cars and trucks have been placed in ERF. Observers near the flats radio the position of the hit in relation to targets. Various weapons have been fired into the salt marsh impact area over the years; the primary ones include 60-, 81- and 107-mm mortars and 105-mm howitzers (Table 4). The howitzer rounds consist of a cartridge case containing propellants, a projectile containing one of several munitions and a detonation fuse (Fig. 8). The fuse can be set to burst on impact with the ground or in the air.

When a gun section at the firing point receives a mission to fire a projectile such as the howitzer types in Figure 8, the following procedure is used: 1) select the appropriate projectile, 2) cut the correct charge of propellant and place the unused propellant to the rear of the gun section for burning at a later time, 3) attach the projectile to the cartridge case, 4) select and attach the appropriate fuse to the projectile, 5) set the appropriate deflection and quadrant (aiming) on the howitzer and 6) fire.

Types, chemistry and toxicity of munitions

Three types of munitions have been fired into Eagle River Flats. These include high explosives, smokes (white phosphorus or hexachloroethane–zinc mixture) and illumination flares (Table 4). During the 40 or more years the ERF has been in use as an impact range, more than a hundred thousand rounds of ordnance have been fired into it. However, it is impossible to compile an accurate record of the number of rounds fired because Range Control records only date back to 1987. An example of the various types of rounds fired is shown for the short period from April to December 1989 (Table 4).

High explosives

Projectiles containing high-explosive compounds are fired from 105-mm howitzers (Fig. 8a) and 60-, 81- and 107-mm mortars. When these hit the ground, the projectile

Table 4. Summary of rounds fired into ERF between April and December 1989.

Projectile	*Type*	*Number of rounds*
60-mm mortar	High explosive	1983
	White phosphorus	106
	Illumination	146
81-mm mortar	High explosive	1520
	White phosphorus	105
	Illumination	94
105-mm howitzer	High explosive	2173
	White phosphorus	27
	Illumination	459
	Hexachloroethane	132
107-mm mortar	High explosive	96
	White phosphorus	36
	Illumination	27
Total		6904

Table 5. Number of white phosphorus rounds fired into ERF between January 1987 and February 1990.

	Number of rounds per calendar year				*White phosphorus*
Projectile	*1987*	*1988*	*1989*	*1990*	*weight per projectile (kg)*
60-mm mortar	187	57	135	29	0.34–0.35
81-mm mortar	287	210	120	29	0.73–1.86
105-mm howitzer	72	35	38	18	1.77

explodes, creating a crater and spreading fragments of steel about the flats. The projectile contains high explosives and uses fragmentation and the blast effect to produce casualties.

High-explosive rounds include one or more of the following chemical components: TNT (1,3,5-trinitrotoluene), RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) or HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine).

The toxicities of TNT and other nitroaromatics have been studied in humans, fish, invertebrates and algae (Burrows et al. 1989). Toxicity data for waterfowl are nonexistent. In humans, exposure to nitroaromatics is manifested by changes in blood. Prolonged exposure results in methemoglobinemia and aplastic anemia. Chronic exposure also leads to toxic hepatitis, which can be fatal. Nitroaromatics may cause central nervous system intoxication (U.S. Army 1984).

In humans, acute exposure to RDX causes convulsions and unconsciousness. Seizures are followed by a period of stupor, delirium, disorientation and confusion, then gradual and complete recovery. Lethality data have been compiled for other mammals (Etnier 1986); oral LD50 values of about 80 mg/kg in mice and 120 mg/kg in rats are reported. Death in these animals is preceded by gasping and convulsions. HMX also hyperstimulates the central nervous system but at much higher doses.

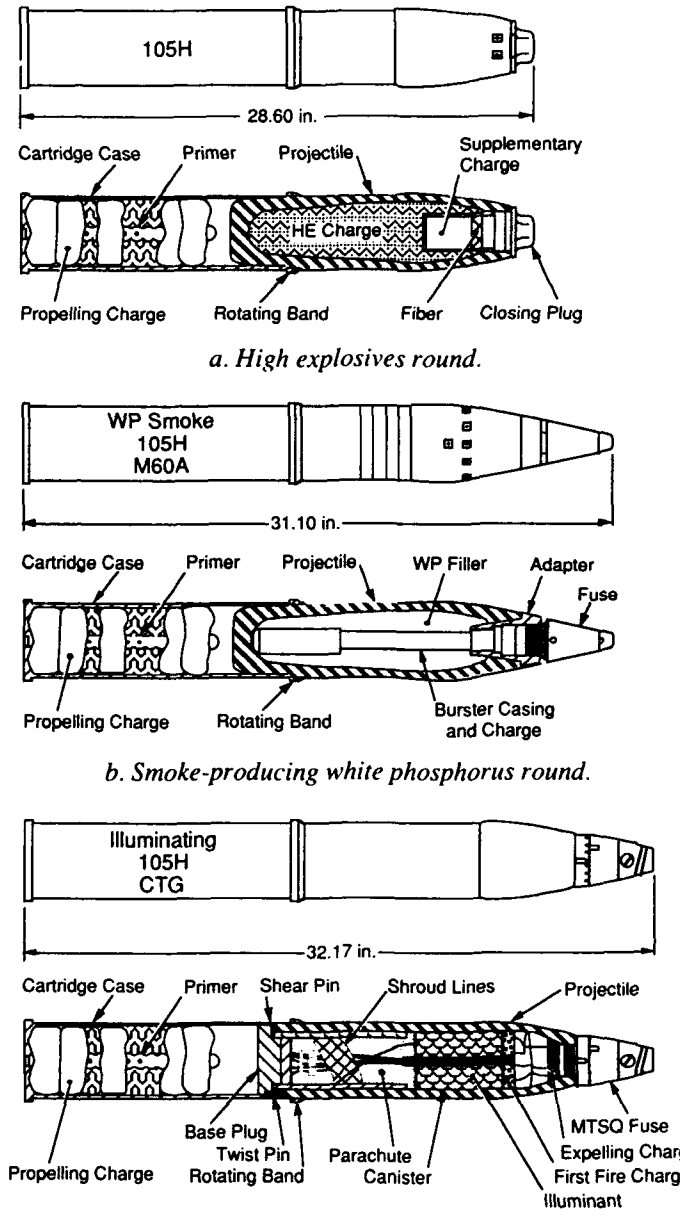
Smoke

Smoke projectiles (Fig. 8b) are fired into the flats by 105-mm howitzers or by 60-, 81- and 107-mm mortars. Smoke rounds contain either white phosphorus or HC (hexachloroethane–zinc mixture).

White phosphorus is the most reactive of the three allotropes of elemental phosphorus (white, red and black). Its molecular structure is that of a regular tetrahedron with a phosphorus atom at each apex, so its molecular formula is P_4 and its molecular weight is 124. It is a wax-like solid that ignites spontaneously in air at 30°C. White phosphorus reacts with oxygen to form various phosphorus oxides, depending on the amount of available oxygen. In the presence of excess oxygen, P_4O_{10} forms, which is hygroscopic and produces a dense white cloud (Yon et al. 1983).

Prior to firing, the white phosphorus projectile can be set to burst in the air or on impact with the ground. Once the projectile bursts, the white phosphorus is scattered, becomes exposed to the air, begins to burn and creates an intense white smoke. If the white phosphorus is immersed in water, it will immediately cease burning until it is exposed to oxygen again. An estimate of 975–1630 kg of white phosphorus was fired into ERF during 1987–1990, based on the number of rounds fired and the weight of white phosphorus per round (Table 5).

White phosphorus is highly toxic to humans by inhalation, skin contact or ingestion. White phosphorus smoke, containing primarily polyphosphoric acid, is an irritant to the respiratory tract of humans at concentrations of 188 mg/m^3 for five minutes (Spanggord et al. 1985). Symptoms of acute toxicity in humans are characterized by three stages over a few days. First, severe gastrointes-



a. High explosives round.

b. Smoke-producing white phosphorus round.

c. Illumination round.

Figure 8. Three types of 105-mm howitzer shells and projectiles fired into Eagle River Flats impact area.

tinal irritation occurs soon after ingestion. Depending on the dose, death or a latent period lasting a few hours to a few days may follow. Systemic effects observed in the third stage include abdominal pain, vomiting, jaundice and convulsions, followed by death. Fatty degeneration of the liver is the most common histopathological evidence of white phosphorus poisoning (Murphy 1986). The ingestion of 1 mg/kg of body weight can be lethal. Studies have also shown that white phosphorus is highly toxic to ducks, with an acute dose of only 1.5–3.0 mg/kg (Coburn et al. 1950). In cases of acute poisoning, ducks died over a few hours. Their symptoms included holding the head erect and swaying from side to side, violent convulsions and sudden death. In the field cases reported by Coburn et al. (1950), the "appearance of being drunk" and loss of coordination were seen. Gross pathological observations indicated dark congested livers and kidneys and other visceral organs. However, the behavioral and pathological observations are not specific enough nor related to individual dose levels and times of death to be of great diagnostic benefit.

HC smoke contains or releases upon deployment primarily zinc chloride and aluminum oxide. Unreacted compounds and by-products include: hexachloroethane, hexachlorobenzene, carbon tetrachloride and phosgene. Except for phosgene, these compounds are toxic by ingestion and primarily affect the liver. Phosgene is a poison by inhalation and results in pulmonary edema.

Illumination rounds

Illumination rounds are fired from 105-mm howitzers and from 60-, 81- and 107-mm mortars. Illumination projectiles consist of an aluminum canister, a magnesium flare attached to a parachute, and a fuse (Fig. 8c). Once the illumination projectile is fired, the fuse will function in the air, causing an expelling charge to shear off the base plate of the projectile and expel a magnesium flare attached to a parachute. The illumination canister and parachute assembly are deployed over a target to illuminate the target area. The flare will continue to burn on the ground or in water. There is no estimate of the total number fired into the flats, but the cannisters are scattered about the surface and are easily found. Ingestion of magnesium rarely causes ill effects except in individuals with depressed renal function (Goyer 1986).

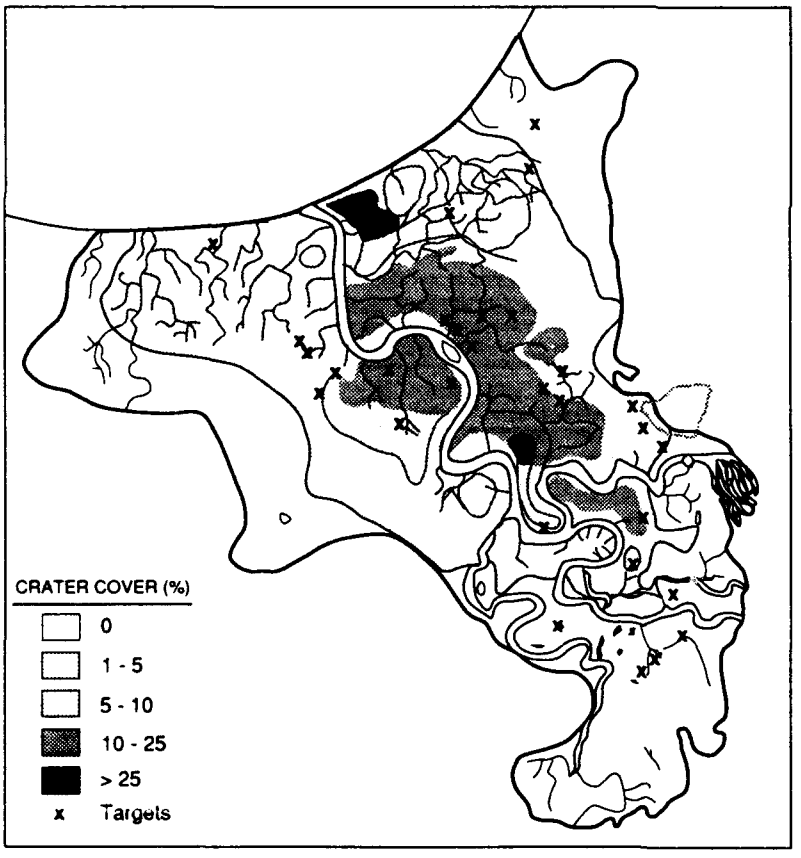


Figure 9. Distribution of explosion craters, showing the percentage of the salt marsh surface covered.

Propellants

Propellants in the form of multiperforated cylinders (grains) are contained in small bags in the shell casing (Fig. 8). The number of propellant bags used to fire a projectile depends on the distance to the target. Under normal circumstances the propellant components would be entirely consumed during the firing of the artillery shell at the firing point and should not be present in the impact area where the artillery projectile lands and explodes. However, surplus propellants are frequently burned at the firing point or are destroyed later in an ordnance disposal area. Such an ordnance disposal area borders a portion of the ERF salt marsh, so propellants are included in this discussion.

The major component of the propellant is the M1 mixture containing the following compounds (U.S. Army 1984): 85 parts nitrocellulose, 10 parts DNT (2,4-dinitrotoluene), 5 parts dibutylphthalate and 1 part diphenylamine.

While nitrocellulose is not considered to be toxic (Dilley et al. 1975), 2,4-DNT and its associated manufacturing contaminant 2,6-DNT are toxic. Acute poisoning of rats from either isomer results in ataxia, respiratory depression and death within 24 hours. Reported lethal doses for rats range from 270 to 2000 mg/kg body weight for 2,4-DNT and 180 to 1000 mg/kg for 2,6-DNT (Etnier 1987).

Explosion craters and associated features

Evidence of the long-term use of the flats as an artillery impact range includes thousands of craters, junk vehicles used as targets, pieces of shrapnel and occasional unexploded ordnance.

Craters range in diameter from 1.5 to 2.5 m, with depths up to 0.5 m. Fresh craters have a sharp rim and are the deepest, while older craters have a more subdued topography. During 1990 many craters remained water filled, and high-water salinities up to 25 ppt were measured in them during May.

Craters from artillery shelling are located throughout the flats but are concentrated in certain areas, presumably in relation to target positions. Figure 9 shows the crater coverage as mapped from aerial photographs. About 70% of ERF has less then 3% crater cover; however, 10% of the area has 15–25% crater cover. A few small areas have as much as 50% crater cover. Crater coverage expresses the intensity of past bombardments in various areas of the flats and may indicate where residues from exploded artillery shells might be concentrated. Based on the average crater size and the crater area map, the total number of craters on ERF is estimated to exceed 100,000.

At least 40 derelict and surplus military vehicles have been placed in the flats over the years to serve as targets for artillery shelling (Fig. 9). These vehicles were airlifted into the middle of the flats by helicopter.

Explosion of most projectiles results in the scattered iron fragments that could be ingested by waterfowl. The iron staining of the gray mudflats during August was particularly striking. Because of the large number of rounds fired into the flats, there are an estimated 10,000 unexploded or partially exploded ordnance projectiles (10% of 100,000).

Explosive ordnance disposal site

Along the eastern edge of ERF is a large gravel pad that has been used as an explosive ordnance disposal (EOD) site (Fig. 10). The gravel pad is approximately 2 m thick and was placed as fill into the edge of the marsh. Aerial photos from 1956 show the edge of the pad in approximately the same location as at present. The surface of the EOD pad is marked with many craters and is littered with the remains of surplus and outdated munitions that have been blown up over the years. Along the bottom edge of the pad, numerous Nike rocket motor casings, junk cars and scrap metal can be found.

Surplus and outdated munitions are disposed of by either burning or explosion. The proper method for disposing of artillery shells is to separate the projectile from the propellant casing, blow up the projectile with explosives and burn the propellant separately. If the entire shell is blown up, incomplete destruction of the shell occurs. The high explosive explodes so fast that propellent grains may be blown upward and outward before they have a chance to ignite.

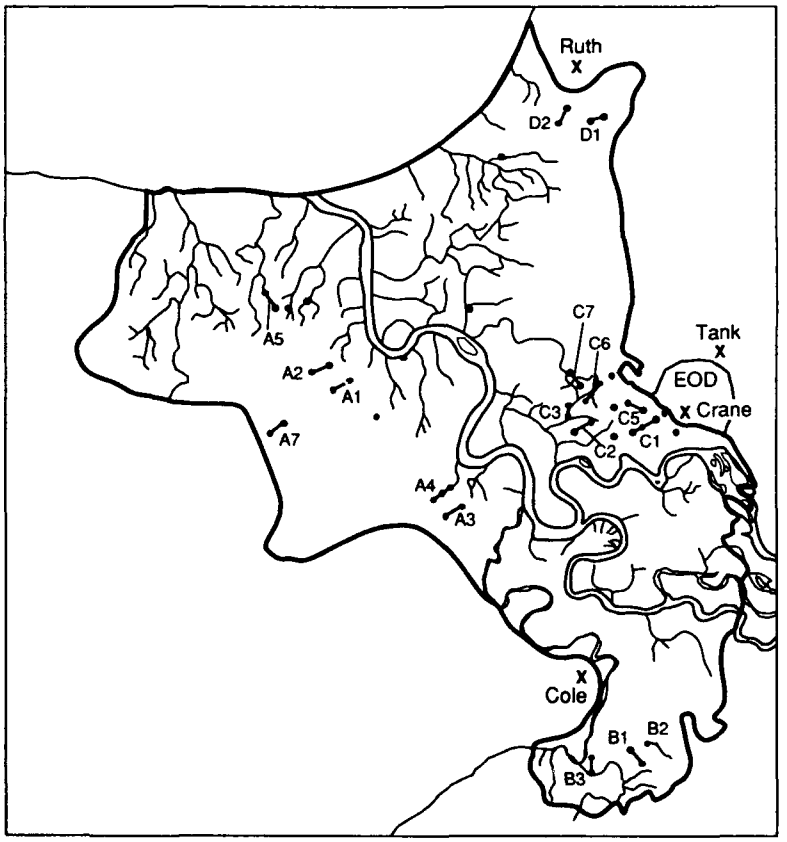


Figure 10. Locations of 100-m-long transects established during the spring of 1990 for sampling sediments and water mainly associated with explosion craters in ERF. Also shown are the locations of survey control points used to survey sample sites (x).

METHODS

Salt marshes are complex and dynamic ecosystems with temporal and spatial changes in environmental conditions. Our study was therefore designed to measure the environmental conditions under which toxic chemicals might be stored or distributed within the salt marsh ecosystem. The types, amounts and toxicity of munitions used in Eagle River Flats were reviewed through records, interviews and literature. Sediments and water were sampled for munitions residues during the spring and fall 1990 waterfowl migrations. In addition, during 13–16 August and 10–15 September, a toxicologist (B.D. Roebuck) and an avian biologist (Dr. Leonard Reitsma) from Dartmouth College observed ducks and collected tissues of individuals that they saw die with violent convulsions. In November 1990, mallard ducks were gavaged with two munitions compounds found in ERF, and their behavior and tissues were analyzed at the Dartmouth Medical School Animal Resources Center.

From the onset of the sampling program, the need to precisely locate sampling sites and manage the analytical results were considered important. We wanted to be able to return to any location where a sample tested positive for munitions residue and be able to intensively resample at the same site. In addition we needed precise coordinates to use a Geographical Information System (GIS) to manage and display sample site locations, chemical test results, vegetation and habitat, and important physical features.

The locations of sampling sites and salt marsh features, as well as the analytical results, were placed in a spatial database using version 3.1 of the Geographical Resources Analysis Support System (GRASS) GIS software developed by the U.S. Army Corps of Engineers Construction Engineering Research Laboratory. This software was used to manually digitize information from the 1:4800 base maps prepared in February 1983 for Fort Richardson and Elmendorf Air Force Base. To use GRASS, coordinates from these maps were converted to Universal Transverse Mercator (UTM) coordinates by personnel at the U.S. Army Corps of Engineers, Alaska District (AK Dist, COE). Information obtained from the maps and entered into the database included the position of Eagle River, intermittent streams, the EOD area and the Knik Arm shoreline. The locations of all samples taken during the initial phase in May 1990 and intensive sampling in August 1990 were surveyed and entered into the database using their coordinate values.

Unrectified color aerial photography acquired in September 1984 and October 1986 at a scale of 1:60,000 was used to define the boundaries of the study area and the density of craters in the impact area. Unrectified color infrared aerial photography at the same scale was photointerpreted to identify vegetation zones, which were also entered into the database.

Location data have been used to produce the maps in this report and are available for additional analysis to determine the relationships between concentrations of potentially toxic materials, suspected source areas and processes that may be responsible for their movement or storage.

Precisely locating scattered sample points throughout the two-mile-wide by two-and-a-half-mile-long area of the ERF presented many challenges. A survey of Ft. Richardson had been conducted in 1983 and 1:4800-scale maps prepared by the AK Dist., COE. CRREL therefore asked the AK Dist., COE to provide a survey crew to assist the CRREL sampling team during the spring study.

The initial approach (during the spring waterfowl migration) was to extensively sample sediment and water in areas A, B, C and D and quickly test or screen these samples in the field for TNT and RDX using methods developed at CRREL (Jenkins 1990, Walsh and Jenkins 1991). Based on the results of the spring analysis of sediment and water from throughout the flats, an intensive fall sampling effort was conducted in area C close to the EOD pad. Observations and collections of feeding, dying and dead ducks were also concentrated in this area during two periods (13–16 August and 10–15 September).

Spring extensive sampling of sediment and water

The sampling program in May was designed to extensively sample sediment and water in a variety of sites within ERF. Our initial hypothesis was that munitions residues (TNT and RDX), if present in ERF, should be located in or next to the explosive craters that dot the surface of the salt marsh. Incomplete combustion upon impact with the wet sediments or water might result in contamination with these compounds. Therefore, most of the sediment and water samples collected during May were from these craters. Because of restrictions against digging into the bottoms of water-filled craters, we were only able to obtain surface sediments 0–10 cm deep in these craters.

Site selection and access

We used an Army UH-1H helicopter provided by Ft. Richardson to gain access to areas A and B. Areas C and D were sampled mainly by foot or canoe from the north side of ERF. In all cases the sampling party was escorted by EOD personnel because unexploded or dud ordnance was a concern. While walking in the impact area, everyone wore snowshoes to reduce ground pressure, which might cause detonation.

A large-scale photo mosaic of the flats was used in the field to help orient the sampling party and to choose

appropriate sampling transects. This mosaic had an overlay with the mapped densities of craters marked. These crater densities express the intensity of past bombardments in various areas of the flats and may indicate where any residues from exploded artillery shells might be concentrated.

Several 100-m-long sampling transects were laid out within each area. Transect endpoints and other sample locations were marked using 4-ft orange survey lath marked with the sample or transect number so that any sample point could be relocated and resampled in the future. Samples of water and sediments were obtained in craters or other features at recorded distances between these endpoints.

Surveying of sites

The locations of the beginning and ends of these transect lines were surveyed by the Alaska District survey crew. Three permanent survey control points, with known coordinates and elevations, were already established on high points around the perimeter of ERF (Fig. 10). "Ruth" is located on the bluff overlooking area D near the northeast edge of the flats. "Point Cole" is located on the southwest side overlooking area B. "Point Tank" is at the observation point overlooking the EOD pad and area C. A fourth control point, "Pt. Crane," was surveyed and established on the edge of the EOD pad, immediately adjacent to area C. Almost all areas of the flats were visible from at least one of these points. The survey points were used to provide location and elevation control for the survey of sample points throughout the flats.

The survey crew set up at the survey point that provided the best view of the area being sampled at the time. A theodolite and a distance measure device (DME) were set up directly over the survey point monument. The instrument was backsighted to another of the control points and the known azimuth between the two points entered. The sampling party carried a range pole of known height with a three-prism reflector on top. At each sample point the theodolite and DME was sighted on the range pole held by a member of the sampling party, and the azimuth and distance to the sample point were determined. Based on the azimuth and distance from the control point, X and Y coordinates for the sample point could be calculated. Horizontal accuracies are on the order of ±0.05 ft. Elevations of the sample points were determined based on the vertical angle and distance between the control and sample points. Because of the long distances being shot from the control points (~5000 ft) and the shallow vertical angles, the accuracy of the elevations determined for the sample points is low (only ±0.25 ft).

Sample collection

At each sample point, separate samples of sediment and water were collected. Sediment was scraped from the top 10 cm of the surface and placed in I-Chem 16-oz wide-mouth jars, cleaned by protocol A (detergent wash and rinse; acid, deionized water and solvent rinse; oven drying; capping and packing). Water samples were collected from standing surface water at the site. At a few sites where there was no surface water present nearby, near-surface groundwater draining into the sampling hole was collected. The water samples were placed in I-Chem 1-L amber glass bottles, cleaned by protocol A. Field notes were made on sample locations and site conditions such as vegetation, soils and water depths.

In addition to the sediment and water samples collected in jars for the analysis of explosives, 10 bulk sediment samples were collected to assess the subsample heterogeneity. These samples were collected in large (3-L) Rubbermaid containers and frozen upon receipt at CRREL. Subsamples were taken from each and analyzed for explosives.

Sample treatment and handling

Samples from ERF were immediately taken to a nearby field laboratory. The salinity and pH of each water sample were measured. Salinity was measured using a Beckman Industrial Solu Bridge, Conductivity Bridge CEL-G20, K-20.0. Measurements of pH were made using a Hach One Portable pH Meter. A 20-g sediment subsample and 500 mL of the water sample were used in the screening field tests for munition residues, and the remaining sample was returned to the CRREL laboratory. Here each sediment sample was air-dried in an 8-inch aluminum pie pan. The water samples were maintained at 4°C until analysis.

Field screening tests for munitions

Since RDX and TNT are the two explosives most commonly found in munitions-contaminated soils, we used field screening procedures specifically developed for detecting these two compounds. Details of these colorimetric procedures are given elsewhere (Jenkins 1990, Walsh and Jenkins 1991), but a brief description follows.

For each sediment sample, a 20-g subsample of undried sediment was extracted with 100 mL of acetone by manually shaking it for three minutes. The extract was filtered and an aliquot removed for the TNT test. TNT was detected by the addition of a strong base (KOH), which results in the production of the red-colored Jackson–Meisenheimer anion. Absorbance was measured at 540 nm using a Hach DR/2000 battery-operated spectrophotometer. Trinitrobenzene (TNB) is also detected by this procedure.

Table 6. Certified Reporting Limits (CRLs) for water and soil analyses for explosive compounds.

Analyte	*CRL for soil (µg/g)*	*CRL for water (µg/L)*
HMX	2.15	ND*
RDX	1.03	0.36
TNB	0.24	0.51
DNB	0.12	0.17
Tetryl	0.65	ND
NB	0.11	0.12
TNT	0.24	0.15
2-Am-4,6-DNT	0.11	0.27
4-Am-2,6-DNT	ND	0.34
2,4-DNT	0.07	0.16
2,6-DNT	0.16	0.22
o-NT	0.24	ND
p-NT	0.22	0.93
m-NT	0.25	ND

* ND =not determined

For the RDX test an aliquot of the filtered acetone extract was passed through an ion-exchange resin to remove nitrate and nitrite. The extract was acidified and mixed with zinc dust, thereby forming nitrous acid, which was then detected using a Griess color-forming solution. A pinkish to rose-colored solution indicates the presence of RDX. The absorbance at 540 nm was measured. Other nitramines (such as HMX) and nitrate esters (such as nitroglycerine and PETN) are also detected with this procedure.

The absorbances measured for both these procedures were converted to analyte concentrations in terms of µg/g based on the response from calibration standards.

Water samples were screened for RDX and TNT using the same color-forming reactions used for the soil procedure. A 500-mL water sample was preconcentrated using a solid-phase extraction cartridge. TNT and RDX are retained on the cartridge, while inorganic salts are not. The cartridge was rinsed by deionized water and eluted with acetone. The acetone extract was split into two aliquots. Strong base was added to one aliquot to detect TNT; the other aliquot was reduced with acetic acid and zinc and mixed with Griess reagent to detect RDX.

Laboratory analytical chemistry

Water and sediment samples were analyzed at CRREL using liquid chromatographic procedures. A 10.0-mL aliquot of each water sample was mixed with 0.10 mL of methanol prior to filtration through a 0.5-µm filter unit. An 1100-µL aliquot was injected onto an LC-8 analytical column eluted with 2.0 mL/min of a ternary eluent composed of 70.7% water, 27.8% methanol and 1.5% tetrahydrofuran. Detection was by UV (λ = 244 and 210 nm). Detection limits for this procedure are given in Table 6.

Sediment samples were analyzed by USATHAMA Standard Method SM02 (Jenkins et al. 1989). Each sediment sample was air-dried to constant weight, and a 2.0-g subsample was extracted with acetonitrile for 18 hours in an ultrasonic bath. A portion of each extract was diluted with aqueous calcium chloride to flocculate suspended particles. The extract was further clarified by filtration through a 0.5-µm filter unit, and a 100-µL aliquot was injected onto an LC-18 analytical column eluted with 1.5 mL/min of a binary eluent composed of 50% methanol and 50% water. Analytes were confirmed on an LC-CN column eluted with the same eluent. Detection was by UV (λ = 254 nm). Certified reporting limits for this procedure are given in Table 6.

Fall sampling of sediments

Because the spring sampling of sediments and water indicated the presence of munitions compounds only adjacent to the EOD, the fall sampling concentrated on intensive sampling along the EOD area and out into the salt marsh in area C (Fig. 11). Appendix A contains a list of the 172 sediment samples collected during the fall.

Figure 11. Locations of fall 1990 transects in area C, where 172 sediment samples were collected to test for munitions.

Selection and location of sample sites

To provide location control for sampling in the vicinity of the EOD pad in area C, a baseline was established along the edge of the EOD pad, and sampling lines were laid out at right angles to the baseline into the flats. Samples were taken along these right-angle lines at various distances based on local site conditions. Because of the more localized sampling area, a separate survey crew was not required in August to locate the sample points. Point Crane, a survey control point with known coordinates, was used as the point of origin for the baseline. Lines were laid out in either direction from the control point, the distances measured by taping, and points or stations marked every 200 ft. The baseline doglegged at the 8+00 and the 14+00 ft stations to more closely follow the edge of the EOD pad. Distances from the baseline to individual sample points along the sampling line were determined by stadia. A theodolite was set up over each station point on the baseline, and readings were made on a stadia rod carried by the sampling party.

The azimuths of the baseline legs were determined by measuring the horizontal angle from the known azimuth between Point Crane and Point Cole and the baseline running through Point Crane. Based on the known location of Point Crane, the known azimuths of the baselines, and known distances to each station and each sample point along the right angle lines, X and Y coordinates were calculated for all stations and sample points tied to the baseline. Elevations were also surveyed for all sampling points.

Additional samples were also taken every 50 ft along the edge of the EOD pad and shoreline from stations 2+00 to 20+00. All sample locations were marked using 4-ft orange survey lath marked with the sample number so that any sample point could be relocated and resampled.

Collection of samples

Only sediment samples were collected because we reasoned that bottom feeding by dabbling ducks would be the most likely pathway for ingestion of toxic compounds. At each sample point, samples of sediment were obtained from 0–30 cm below the surface and placed in I-Chem 16-oz wide-mouth jars, cleaned by protocol A. Sampling techniques varied depending on site conditions. Where there was a thick sod, a shovel was used to cut through the tough organic mat to reach the underlying sediment, usually at a depth of 30 cm. A representative sample of sediment and organic material was collected along the length of the shovel cut from 30 cm to the surface. In the soft sediment bottoms of the shallow ponds, surface sediment was collected by scraping to a depth of 10 cm into the sediment over as wide an area as possible (1 m^2).

Sample treatment and handling

Sediment samples were returned to a nearby lab set up at the Alaska Dist, COE office at Elmendorf AFB. The salinity of the standing water in the jar was measured with the same salinity meter as that used in the spring. In addition, the redox potential was measured using a Hach One Portable pH Meter (in millivolt mode) equipped with a Hach Oxidation–Reduction (ORP) electrode. Redox potential measurements are used to classify soils as oxic, suboxic or anoxic. Redox potentials less than +118 mV indicate anoxic conditions (Sposito 1989). The oxidation state of the sediments is considered important to the production and storage of various chemicals in wetland soils.

In the laboratory, half of each sample was air-dried in a pie plate and the remainder was kept tightly sealed and refrigerated. Two subsamples of the air-dried portion were weighed out. One subsample was extracted with acetonitrile for analysis of explosives. The other subsample was tested for aqueous soluble orthophosphate using a Hach kit procedure (PhosVer 3-Ascorbic Acid Method). Since a single sediment sample collected near the EOD in the spring suggested the presence of white phosphorus, it was desirable to screen for white phosphorus or a related compound such as orthophosphate, which forms when white phosphorus is exposed to air and water.

Analytical chemistry

For the analysis of explosives in sediment samples collected in the fall, the spring analytical method was modified in three ways. The size of the subsample extracted with acetonitrile was increased to 10 g, and the liquid chromatographic column and eluent described above for the May water samples were used. These changes were made since the analytes detected in the May samples were present in trace quantities and were heterogeneously distributed in at least one sample. A larger subsample would not only increase the sensitivity of the method, it would provide for a better representation of the sample as a whole. The column and eluent were changed to provide for the separation of the isomers of DNT. Additionally, only half of each sample was dried. The remaining undried portion was kept tightly sealed in a refrigerator and saved for analysis for white phosphorus. While we were not prepared to analyze for white phosphorus at the onset of the fall sampling, we initiated a literature search to see if an analytical method existed.

Sediment extracts with the highest analyte concentrations were also analyzed by gas chromatography–mass spectrometry. This analysis provided firm confirmation of analyte presence as well as identification of some unknowns. A 1-µL splitless injection was made onto a 25-m (0.2-mm-ID) 5% phenyl methyl silicone fused

silica capillary column. The column was temperature-programmed from 75° to 240°C at 20°C/min. The mass spectrometer was operated in scan mode over the mass range of 29 to 300.

Sediment samples that tested positive for orthophosphate were analyzed for white phosphorus using a procedure adapted from that described in Addison and Ackman (1970). Sample preparation for white phosphorus analysis was carried out inside a glove bag purged with nitrogen. There a subsample of wet sediment was added to 5.0 mL of isooctane in a preweighed vial. Samples were shaken overnight on a wrist-action shaker, then allowed to stand until phase separation. Then an aliquot of the isooctane layer was analyzed. The presence of white phosphorus was tested by gas chromatography–mass spectrometry (GCMS). The same instrumental parameters as those described above for explosives were used, except the mass scan range was changed to a low mass of 29 and a high mass of 150. Quantitative measurement of white phosphorus in the sediment samples was made using gas chromatography with flame photometric detection (GC-FPD) (Addison and Ackman 1970). A 1-µL aliquot of the sediment extract was injected onto a 15-m (0.53-mm-ID) 1% methyl silicone fused silica capillary column. The column temperature was maintained at 75°C for 2 minutes, then increased at 10°C/min to 100°C. Under these conditions, white phosphorus eluted at 7.2 minutes.

Fall observations, collection and analysis of waterfowl

Observations and collections of dying waterfowl were made in area C during two fall migration periods: 13–16 August and 10–15 September. The objectives of these observations were to document the behavior of ducks with regard to their feeding activity and distressed behavior culminating in death and to obtain tissues for histopathologic, chemical and gross analysis.

Waterfowl field behavior

Waterfowl observations were made with spotting scopes and binoculars from shore in August and from a 20-ft-tall blind during September. Ducks on the surrounding shallow ponds were watched until one or more individuals became sick. Stricken birds were approached and their behavior monitored more carefully and recorded with both video and still cameras.

Tissue collection

In August, tissues from three ducks that died suddenly and violently were preserved in buffered formalin for histologic examination. Later these tissues were stained with hematoxylin and eosin, and thin sections were prepared for light microscopic examination. In September four ducks were autopsied immediately after death, and their organs were removed for white phosphorus analysis by gas chromatography. These organs were frozen in dry ice. Samples of heart, liver, intestines, kidney, gizzard contents, fat, brain and muscle (pectoral and gizzard) were collected. A fifth duck was removed sick from the flats in September; it survived for 9.5 hours after the initial convulsions. This teal was frozen and sent to CRREL, where it was autopsied. Tissue samples were immediately homogenized, extracted and analyzed.

In October, task force personnel collected two dead mallards, three dead swans and one dying swan in ERF. The gizzards of the dead birds were removed, frozen and sent to CRREL for chemical analysis. In addition, five green-winged teal were collected in Susitna Flats, frozen and shipped to CRREL to be used as control birds.

Laboratory preparation of tissue samples

The gizzard of each duck and swan collected was opened with a scalpel, and the contents were scraped into a vial. A 5-mL aliquot of isooctane was added, and each sample was extracted as if it were a sediment sample.

Tissue samples were homogenized in 10 mL of degassed water in a Waring blender in a nitrogen-purged glove bag. An additional 10 mL of water was used to rinse the blender and then was combined with the tissue and water in a vial. A 10-mL aliquot of isooctane was added, and each sample was shaken overnight on a wrist-action shaker. To expedite separation of organic and aqueous phases, samples were centrifuged for 30 minutes at 3000 rpm.

Analytical methods

Isooctane extracts of tissue samples were analyzed for white phosphorus by gas chromatography with flame photometric detection (Addison and Ackman 1970) and by gas chromatography-mass spectrometry (GCMS). These tissue extracts were analyzed for white phosphorus using the same procedure as described for sediment samples.

Laboratory toxicity study

Domestic mallard ducks were dosed with one of two chemicals: white phosphorus or 2,4-DNT. The intent of the study was to compare the behavioral symptoms of laboratory ducks treated with a known quantity of the two munitions residues found in ERF with the behavioral symptoms of poisoned birds observed in ERF. Behavior was observed, and blood or tissue samples or both were collected following dosing. Adult mallards were housed in the Animal Resources Center at Dartmouth Medical School in two 1.2- × 2-m rooms connected by a small opening. The temperature of the

room was 19°C, and lighting was kept on a 12-hour light–dark cycle. Ducks were fed a 50:50 mixture of Agway cracked corn and layer pellets. One room contained wood shavings, while the other had a wading pool filled with tap water. The ducks had access to the food and pool at all times.

White phosphorus toxicity study

White phosphorus was dissolved in oil (tricaprylin) prior to dosing each duck. To prevent oxidation of white phosphorus, solutions were prepared under a nitrogen atmosphere. Solid white phosphorus, shipped and stored under water in an airtight container (Aldrich Chemical Co., Milwaukee, WI), was dried by brief immersion in acetone and dissolved in tricaprylin (Fluka AG, Chamische Fabrik). The solution was mixed for one hour at a temperature of 40°C to ensure proper dissolution, and it was stored at 20°C in the dark. The white phosphorus concentration was calculated based on the weight of the solid white phosphorus and confirmed by gas chromatography (GC-FPD). White phosphorus solutions were made at concentrations of 2.3 and 2.8 mg/mL.

Mallards were gavaged with 12 mg of white phosphorus per kg of body weight for a total volume of 5–6 mL of white phosphorus dissolved in tricaprylin. This dose was the same as the largest dose used in the only other study of white phosphorus toxicity in ducks (Coburn et al. 1950). The ducks were then returned to the room in the company of untreated ducks. The behavior of all the birds was closely monitored. Upon observation of repeated and violent convulsive behavior, 45 mg of ketamine was injected into the breast tissue to anesthetize the bird, and the bird was sacrificed for tissue analysis. Autopsy and tissue preparation for white phosphorus analysis was undertaken immediately. Behavioral observations, histological analyses and tissue sample collections for white phosphorus analysis were made on three common mallard ducks fed white phosphorus.

2,4-DNT toxicity study

A slurry of reagent-grade 2,4-DNT (Eastman Chemicals) in tricaprylin was prepared. In two separate experiments a mallard was gavaged with 1000 mg of 2,4-DNT via a tube to the gizzard. The duck was closely observed and its behavior recorded. Canulas were placed into the artery and vein vessels of the left wing to withdraw blood samples after two hours and hourly thereafter. These blood samples were assayed for percent methemoglobin, a form of hemoglobin produced by 2,4-DNT. Methemoglobin cannot carry oxygen; thus, ducks poisoned with 2,4-DNT are deprived of oxygen (anoxic). Pentabarbitol was used to anesthetize and sacrifice the bird.

To determine the percentage of methemoglobin produced in the blood as a result of 2,4-DNT, an assay developed by Smith (1971) was used. The assay measures methemoglobin by spectrophotometric determination at 635 nm and then converts the methemoglobin to cyanide-methemoglobin and remeasures the absorbance at 635 nm. By subtracting the second measurement from the first, the amount of blood methemoglobin is determined. To determine total methemoglobin as a percentage of total blood pigment, oxyhemoglobin is measured by converting it to cyanide-methemoglobin and measuring its absorbance at 540 nm.

RESULTS

Spring analyses of sediments and water

Neither RDX nor TNT was detected in any of the 93 sediment and water samples with the field screening procedures. However, when the samples were analyzed in the laboratory by liquid chromatography, three sediment samples from the area next to the EOD (Fig. 12) were found to contain 2,4-DNT, a component of the

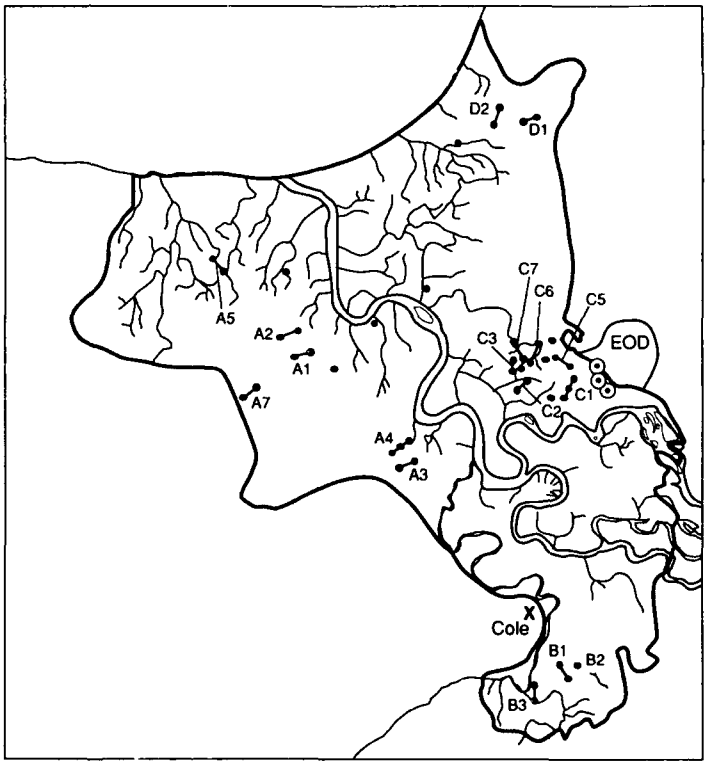
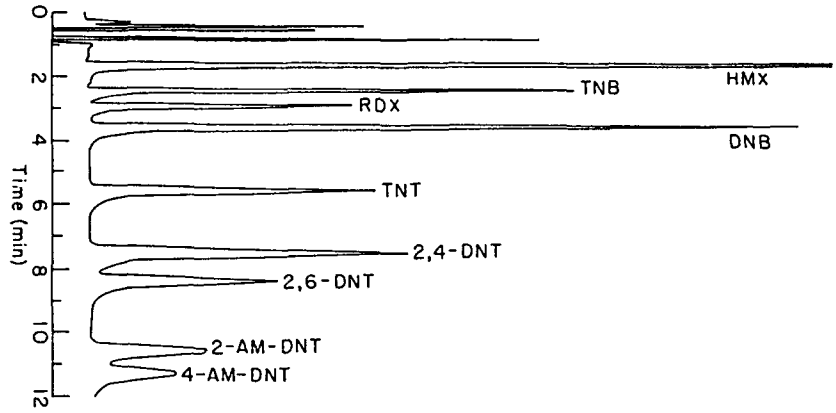
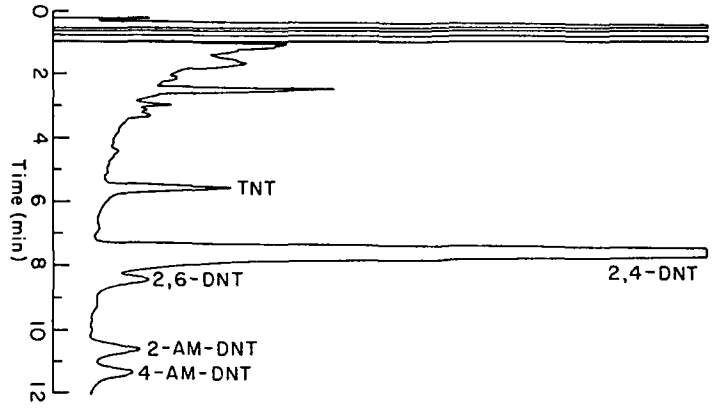


Figure 12. Spring sediment sample transects and three locations where 2,4-DNT was detected (circled dots).



a. Standard solution containing HMX, TNB, RDX, DNB, TNT, 2,4-DNT, 2,6-DNT, 2-Am-4,6-DNT and 4-Am-2,6-DNT.

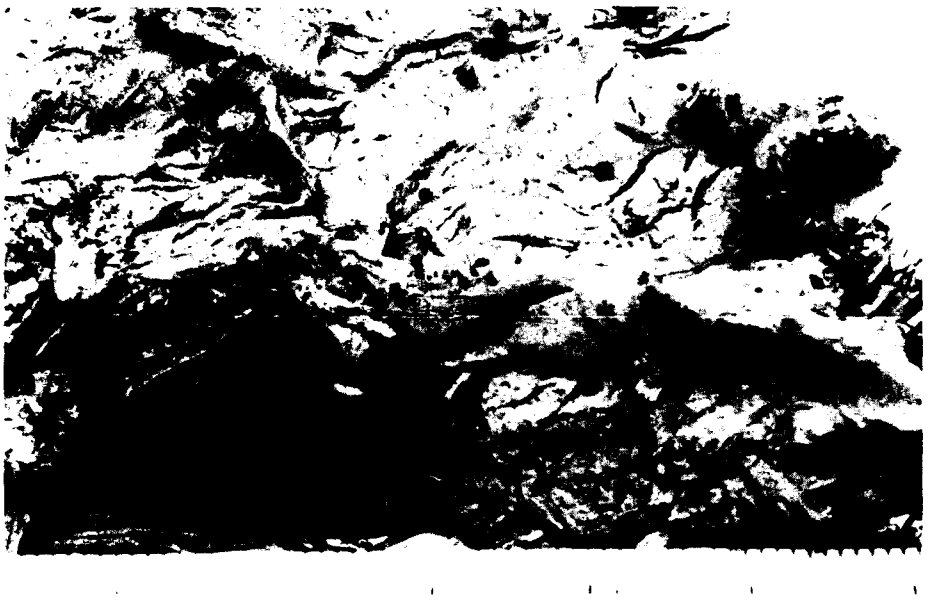


b. Extract of a sediment sample obtained in ERF next to the EOD area.

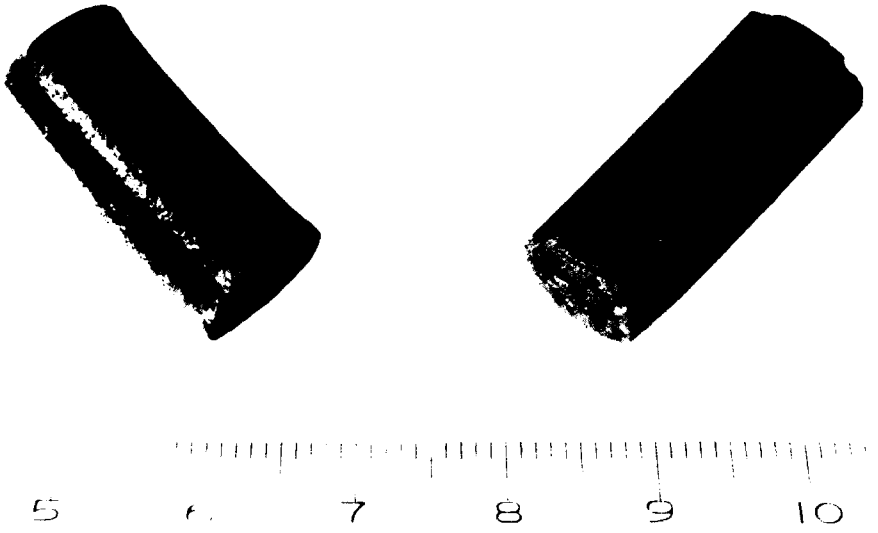
Figure 13. Chromatograms from high-performance liquid chromatography. Each compound has a different and characteristic peak time of emergence from the column.

propellant M1 composition. This contamination would not have been detected using the field screening procedure since it is optimized for RDX and TNT. Two samples contained only trace amounts (0.4–0.5 µg/g), while the levels in the third bulk sample varied with each subsample (0.61, 3.42, 4.82, 18.0 and 27.4 µg/g dry wt). In addition this sample contained other compounds, including 2,6-DNT (0.03–0.89 µg/g), 2,4,6-TNT (0.15–0.50 µg/g) and the TNT reduction products 2-amino-4,6-dinitrotoluene (0.08–0.47 µg/g) and 4-amino-2,6-dinitrotoluene (0.16–0.52 µg/g). An HPLC chromatogram from the calibration standard and sediment extract confirmed the presence of these compounds (Fig. 13). The compounds 2,6-DNT and TNT are byproducts of the manufacture of 2,4-DNT for propellants and as such are present at much lower concentrations. The amino compounds are breakdown products of TNT, which form when a nitro group on the TNT molecule is reduced.

To reconfirm the presence of 2,4-DNT at the site, three additional samples were collected from the same location and shipped to CRREL in late June. Only trace amounts (0.02–0.04 µg/g) of 2,4-DNT were again found in these samples. However, one of these samples gave off a vapor cloud when the container was opened and the sediment stirred. This behavior suggested the presence of a smoke-producing chemical such as white phosphorus (Fig. 14a). Therefore, a portion of the sample was air-dried and tested for orthophosphate (an oxidation product of white phosphorus) using a Hach kit (ascorbic acid, sodium molybdate method). The concentration of phosphate was beyond the range for this procedure, or greater than 225 ppm. On 31 July, Dr. R. Wentsel (Chemical Research Development and Engineering Center, Aberdeen Proving Ground, Maryland) came to CRREL to discuss the environmental fate of white phosphorus, and he called attention to the paper by Coburn et al. (1950) on the oral toxicity of white phosphorus to ducks. The



a. Particles of oxidized white phosphorus, visible as black specks in this dry sediment sample from a deep "hole" in the salt marsh.



b. Propellant grains found on the EOD pad and in the adjacent salt marsh.

Figure 14. Munitions found in ERF. The scale is in centimeters.

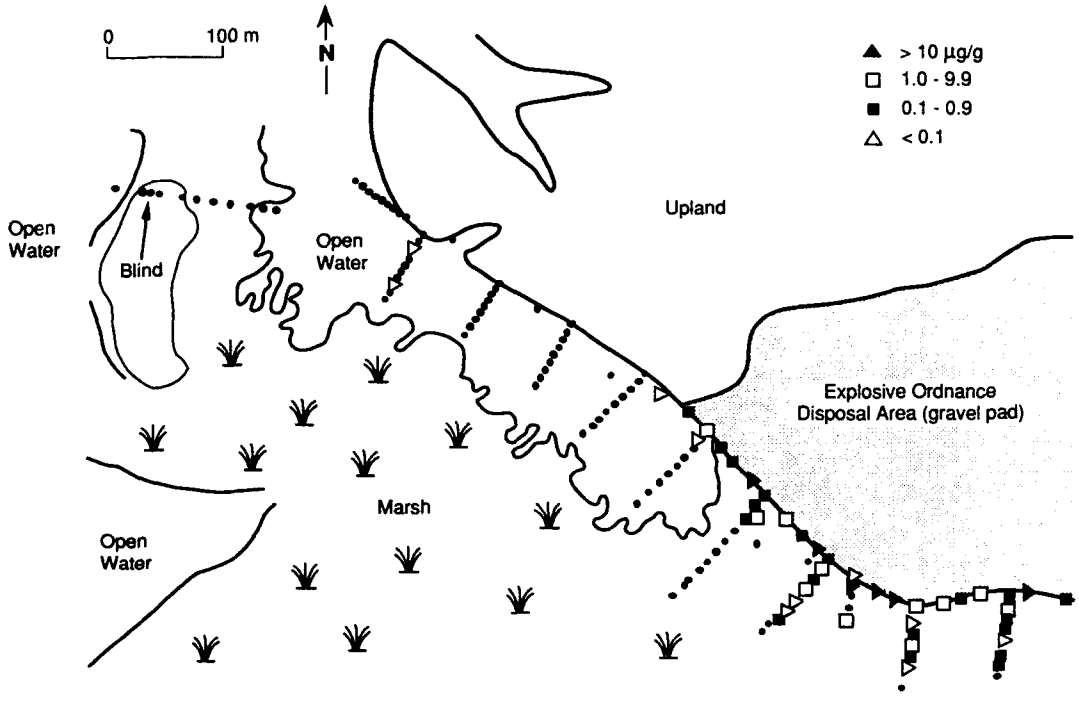


Figure 15. Area C sediment sample sites in relation to the detection of various levels of 2,4-DNT.

presence of white phosphorus in ERF sediments was confirmed in September by GCMS (described below).

Fall analyses of sediments

Out of the 172 samples collected from the salt marsh, 62 were contaminated with 2,4-DNT. All of these samples were collected from along the base of, or in the salt marsh adjacent to, the EOD area (Fig. 15). In most samples with concentrations of 2,4-DNT greater than 1 µg/g, 2,6-DNT and TNT were also confirmed but at much lower concentrations. Also present in some samples were trace amounts of the TNT biotransformation products 2-amino-4,6-dinitrotoluene and 4-amino-2,6-dinitrotoluene.

In the fall, propellant grains (Fig. 14b) were found scattered on the EOD pad and in one deep sediment sample "hole" in the adjacent salt marsh. The acetonitrile extracts of these propellant grains and the sediment samples containing the highest concentrations of 2,4-DNT were analyzed by GCMS (Fig. 16). The mass spectra showed similar compounds in the sediments and grains (Fig. 17), including 2,4-DNT and 2,6-DNT as well as diphenylamine and dibutylphthalate. These compounds are components of M1 propellant (U.S. Army 1984).

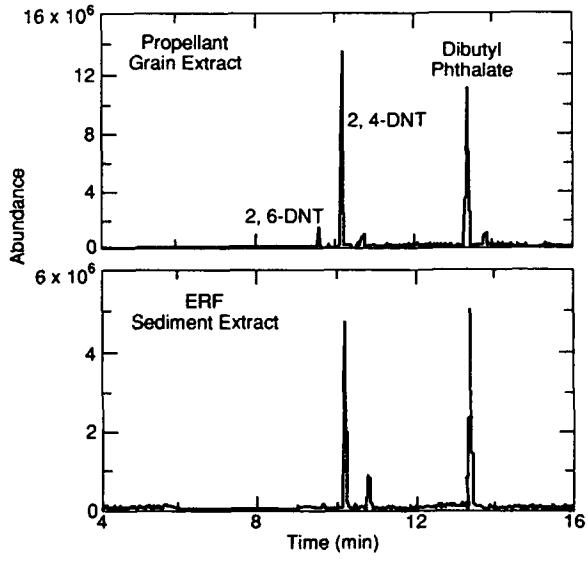


Figure 16. Chromatograms from a gas chromatograph (GCMS) comparing peak retention times of compounds contained in a whole propellant grain found in the ERF salt marsh next to the EOD and a sediment sample collected at the base of the EOD.

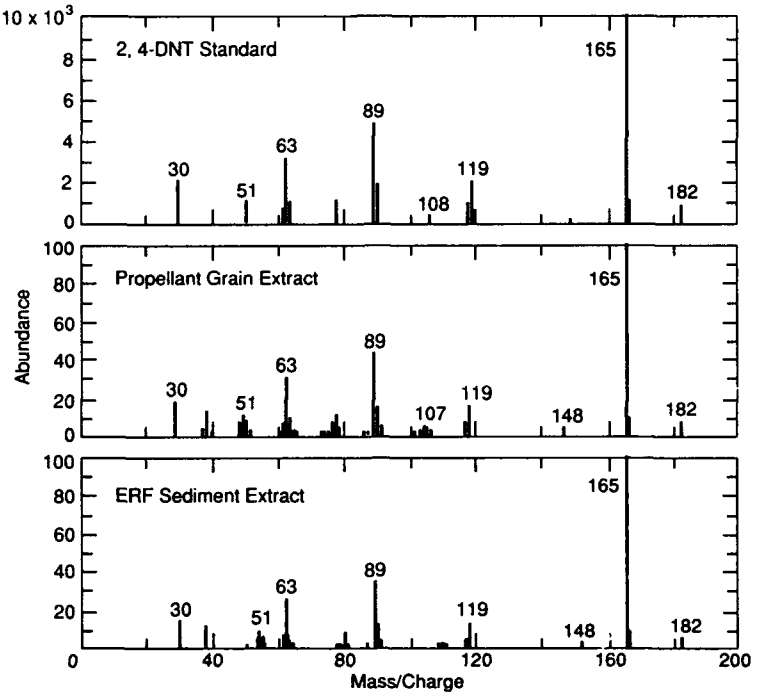


Figure 17. Mass spectra from GCMS analyses in which 2,4-DNT detected from the propellant grain and sediment sample at the base of the EOD (Fig. 16) has been fragmented. The masses for each fragment are printed above each peak.

Of the 42 sediment samples that tested positive for phosphate in the fall (including the smoke-producing spring sample, which tested off-scale for orthophosphate), 17 samples were subsequently analyzed for white phosphorus by GCMS (Fig. 18 and 19). Eight of these samples contained white phosphorus at detectable levels. The presence of white phosphorus was confirmed in the sediments by the mass spectrum (Fig. 20), in which the predominant ion corresponds to the molecular weight of P_4 (124). Quantitative analysis by gas chromatography flame photometry (GC-FPD) showed five samples with trace amounts (0.0004 µg/g), one at 10.2 µg/g (wet weight) and one at 0.18 µg/g.

Tissue analyses of wild birds

Histopathologic examination of tissues (liver, kidney and gastrointestinal tract) from teal observed to convulse and die in ERF were compared with the same tissues from teal collected in Susitna Flats. No obvious microscopic differences were noted. Coburn et al. (1950) noted effects of white phosphorus on tissues, especially liver and kidney, but this was primarily seen grossly during autopsies of ducks dying from acute exposures; histopathological abnormalities were only seen in ducks dying after chronic exposure or a few days after acute exposures.

Tissues from 11 birds (7 ducks and 4 swans) from ERF were analyzed for white phosphorus (Table 7). Gizzard contents and fat tissue were also analyzed in five ducks collected in Susitna Flats. White phosphorus was found in the gizzard contents of all ducks from ERF (Fig. 20) but in none of the ducks from the control area (Susitna Flats). It was also found in the livers of four ERF ducks that died soon after convulsing, and in the fat of a duck that survived for 9.5 hours after the onset of convulsions (Table 7). White phosphorus was not found in any blood samples but did occur in two of four heart samples and two of four kidney samples analyzed from ERF birds. In addition, white phosphorus was found in the extracts of the gizzard contents of all swans collected in ERF and in the fat of three of these swans. The gizzard contents of most of the swans we examined were composed primarily of small pieces of gravel. However, the gizzard of one swan (#3 in Table 7) was full of organic material, primarily sprouting seeds. The mass of white phosphorus found in the gizzard contents of this swan was 11 mg, and the concentration in the fat was 2.0 µg/g.

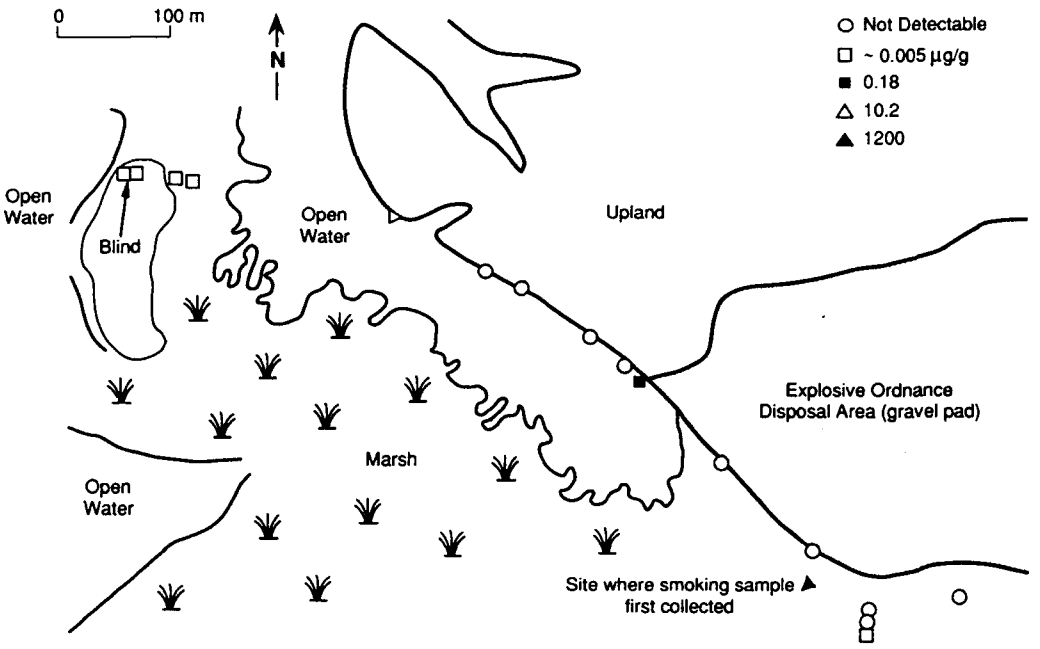


Figure 18. Area C sample site locations showing which samples were tested for white phosphorus and which samples showed nondetectable, trace or significant levels.

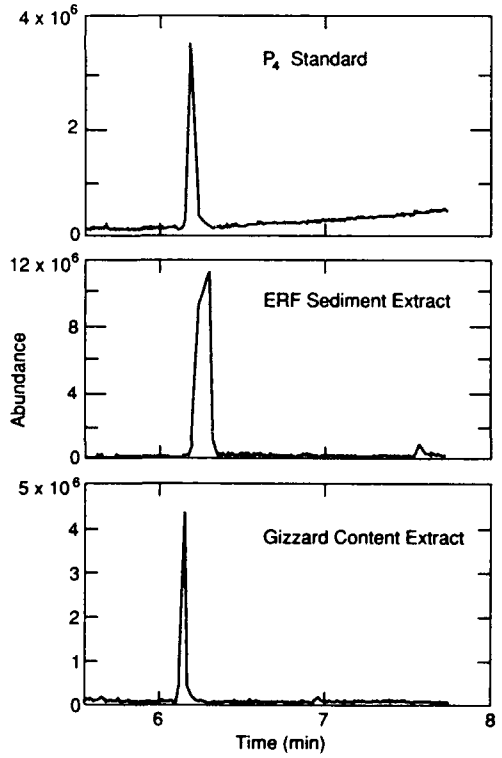


Figure 19. Chromatogram from a GCMS comparing peaks for a white phosphorus standard and extracts of an ERF salt marsh sediment and of the gizzard contents of a pintail duck that died in ERF on 11 September 1990.

Table 7. Concentrations of white phosphorus detected in various tissues and organs of dying and dead ducks and swans collected in ERF during the 1990 fall migration.

Specimen	*Sample no.*	*Type of tissue*	*Mass of tissue (wet weight) (g)*	*Mass of white phosphorus (mg)*	*Concentration of white phosphorus in tissue (mg/g)*
ERF samples					
Pintail	60	Heart	1.7	0	0
(collected	61	Liver	7.1	0.351	0.049
9/11/90)	66	Gizzard contents	1.5	111	74
	71	Intestinal contents	1.3	1.07	0.82
Green-winged	73	Liver	4.6	0.047	0.010
teal (male;	74	Kidney	2.9	0	0
collected	78	Gizzard contents	0.53	0.295	0.56
9/11/90)	83	Intestinal contents	not weighed	0.081	NA
	84	Intestines	10.4	9.8	0.94
Green-winged	96A	Blood	1.7	0	0
teal (female;	96B	Liver	6.3	0.91	0.144
collected	96C	Heart	2.1	0.159	0.076
9/12/90)	96D	Kidney	1.1	0.015	0.014
	97	Gizzard contents	0.15	0.012	0.08
	98	Intestines	not weighed	6.1 6	NA
Green-winged	99	Heart	2	0.389	0.19
teal (male;	99A	Blood	4.4	0	0
collected	100	Liver	8.7	0.411	0.049
9/12/90)	101	Kidney	2.2	0.043	0.019
	110	Gizzard contents	0.17	0.022	0.13
	111	Intestines	16	7.9	0.494
Green-winged	112	Pectoral muscle	35.6	0.059	0.0016
teal (collected	113	Heart	4	0	0
live 9/15/90;	114	Liver	10.4	0	0
survived	115	Intestines	14.7	0.08	0.005
9.5 hours)	116	Kidney	3.5	0	0
	117	Brain	2	0	0
	118	Fat	8.8	0.4	0.045
	119A	Gizzard muscle	11.8	trace	trace
	119B	Gizzard contents	0.67	0.08	0.12
Tundra swan	1A	Gizzard contents	4.4	0.24	0.054
(adult)	1B	Fat	6.9	0	0
	1C	Blood serum	not weighed	0	0
	1D	Whole blood	not weighed	0	0
Tundra swan	2A	Gizzard contents	10.7	0.24	0.022
(immature)	2B	Fat	6.3	2.03	0.32
Tundra swan	3A	Gizzard contents	53.1	11,000	206
(immature)	3B	Fat	6.6	19.2	2.9
Tundra swan	4A	Gizzard contents	1.4	0.085	0.061
(adult)	4B	Fat	9.1	0.93	0.102
Mallard	5A	Gizzard contents	3.1	60.5	19.5
(male)	5B	Fat	0	NA	NA
Mallard	6A	Gizzard contents	5.4	1.5	0.28
(male)	6B	Fat	2.6	0	0

Table 7 (cont'd). Concentrations of white phosphorus detected in various tissues and organs of dying and dead ducks and swans collected in ERF during the 1990 fall migration.

Specimen	*Sample no.*	*Type of tissue*	*Mass of tissue (wet weight)(g)*	*Mass of white phosphorus (µg)*	*Concentration of white phosphorus in tissue (µg/g)*
Controls					
Green-winged teal		Gizzard contents	1.34	0	0
(male; Susitna)		Fat	4.99	0	0
Green-winged teal		Gizzard contents	1.68	0	0
(female; Susitna)		Fat	6.35	0	0
Green-winged teal		Gizzard contents	2.13	0	0
(male; Susitna)		Fat	2.95	0	0
Green-winged teal		Gizzard contents	1.95	0	0
(male; Susitna)		Fat	3.21	0	0
Green-winged teal		Gizzard contents	1.55	0	0
(female· Susitna)		Fat	4.05	0	0

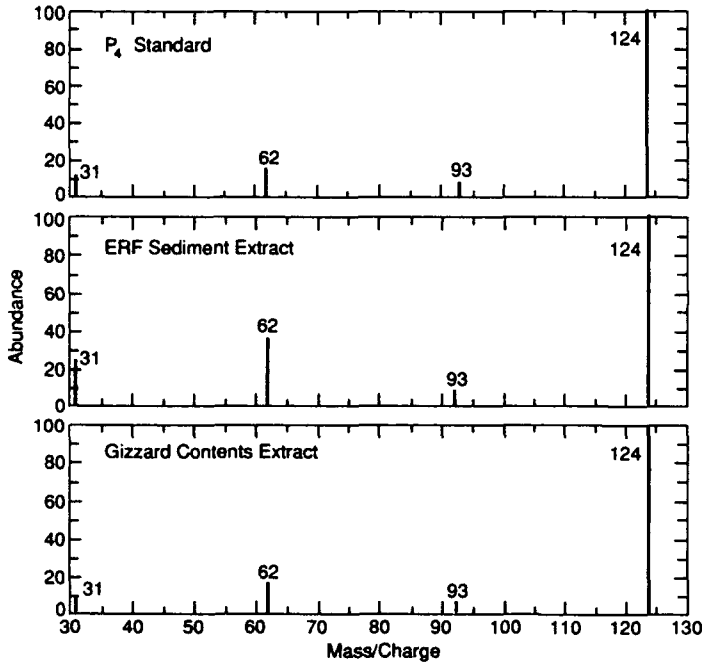


Figure 20. Mass spectra for the white phosphorus standard, the salt marsh sediment sample and the gizzard contents of the pintail shown in Figure 19. The mass spectrum of white phosphorus has a large peak at mass 124, the molecular weight of white phosphorus (P_4). This molecule also fragments into P, P_2 and P_3, which have masses of 31, 62 and 93, respectively.

Field behavior observations

From 10 to 15 September, field observations of ducks were made from a blind in area C. During this time, symptoms associated with the death of six ducks were closely monitored from the blind. The general progression of symptomatic behavior ranged from lethargy, hiding in dense vegetation, head-rolling back and forth across their back, swimming in circles and violent convulsions followed by death (Fig. 21). The behavior of laboratory treated ducks was similar, although the length of time from the early symptoms to the onset of convulsions and death varied. The most characteristic behavior of sick ducks involves neck-writhing or rolling while the top of the head is touching the back of the bird (Fig. 21b), swimming in tight circles, and convulsions (Fig. 21c), with earlier signs of sickness difficult to detect.

One individual was followed closely for at least 45 minutes prior to convulsions. This individual was with five other green-winged teal and about 90 wigeon. The other teal were either actively foraging or resting with their bills on their backs (a typical resting pose). The sick individual was swimming with its neck pulled down, similar to the pose often seen when the temperatures are very low (Fig. 21a). Perhaps the most s iking behavior at this early stage was strong head-shaking. Other ducks usually shake their heads in association with preening behavior and presumably to remove excess water from the head and neck. This teal, however, was not preening, and its bill often splashed uncontrollably in the water when it shook its head. After about 30 minutes, the duck swam to the pool's edge and walked onto land. Shortly thereafter it swam out of view behind a clump of grass and after 10 minutes violent convulsions began.

a. Duck with its head down and feathers out, indicating the onset of symptoms of poisoning.

b. Same duck showing an arched neck and cocked rump prior to convulsions.

Figure 21. Green-winged teal in area C on 12 September 1990 showing symptoms of poisoning.

c. Convulsions just prior to death.

Figure 21 (cont'd). Green-winged teal in area C on 12 September 1990 showing symptoms of poisoning.

Table 8. Distinctive behavioral characteristics observed in three domestic mallards treated with 12 mg/kg white phosphorus and two domestic mallards treated with 1000 mg/kg 2,4-DNT.

Ducks treated with white phosphorus (12 mg/kg)	*Ducks treated with 2,4-DNT (1000 mg/kg)*
Agitation	Frequent drinking
Frequent drinking	Panting/heavy breathing with the bill open
Uncontrolled head shaking	Shivering
Vomiting	Inactivity
Seeking seclusion	Wobbly gait
Lethargy	Sedation and death
Loss of coordination of head and legs	
Rearing back and swaying of head	
Convulsions: wings extended, tail upward, head thrust back	
Death	

Observations suggest that the immediate cause of death often may involve drowning or predation by gulls, eagles or ravens. A convulsing duck can drown because it loses control of its neck so that its bill dips below the surface of the water or because it becomes entangled (as a result of convulsions) in the aquatic or sedge vegetation in which stricken ducks were observed to hide. We prevented two individuals from drowning in order to observe the range and sequence of symptoms and to see if recovery was possible. In two cases, convulsing ducks were attacked by gulls. The gulls made regular checks on the duck flocks at ERF and often sit for extended periods of time where they can observe the flock. When a duck is recognized as sick, both gulls and eagles compete for the stricken duck.

It was difficult to measure the rate of mortality in the vicinity of the blind. Besides the six ducks that we observed, we also found three ducks presumed to have died over the period of observations and saw at least three others carried off and eaten by eagles.

Laboratory toxicity studies

White phosphorus study

After white phosphorus was administered to one mallard, normal activities were observed, including wing flapping, preening, drinking, bathing and frequent movement from pool to floor. Within 75 minutes, violent head shakes with an open beak occurred for 15 minutes (Table 8). For the next three hours, normal behavior was ob-

served, with mild head shakes. Four hours and 30 minutes after administration, uncontrollable head-shaking with an open beak and constant dipping of the bill were observed, followed by languid behavior. The duck apparently showed photophobia by placing its head in a small opening between the rooms and under the pool edge and by closing its eyes. Forty-five minutes later the duck staggered and stretched its neck in small jerking movements. Within five minutes the duck violently convulsed twice. (In this study a convulsion is used to describe a duck with the following characteristics: arched neck and tail with the top of the head resting on the back of the duck and the beak pointing dorsally, wings spread out along its side, open eyes and exposed chest.) After the second convulsion, the duck was injected with ketamine to anesthetize the bird and was sacrificed. A second duck, treated with white phosphorus at the same dosage, behaved similarly but did not exhibit the violent convulsions (though mild convulsions were observed). That duck was sacrificed after 10 hours.

Tissue analysis for white phosphorus in these two ducks revealed concentrations similar to those found in tissues of ducks from ERF (Tables 7 and 9). The highest concentrations were found in the fat, while low values occurred in the brain tissue.

2,4-DNT study

The behavior of the two ducks dosed with 2,4 DNT included inactivity, panting or heavy breathing with the bill open after one to two hours (Table 8). Wobbling gait and shivering occurred at about four hours post-dosing.

Table 9. White phosphorus concentrations in tissues of two domestic mallards dosed with 12 mg white phosphorus per kilogram of body weight.

	White phosphorus concentration (µg/g)			
Mallard	*Liver*	*Fat*	*Breast muscle*	*Brain*
1	0.029	1.22	0.013	0.000
2	0.009	0.39	0.052	0.007

Table 10. Methemoglobin in the blood of a domestic mallard dosed with 1000 mg of 2,4-DNT per kg of body weight.

Time after dosing (hr)	*Methemoglobin (% of total heme)*	
	First mallard	*Second mallard*
0	6	14
2	35	51
3	50	59
4	63	43
5	48	41
6	42	Died

No convulsions occurred, and a quiet death occurred at five to six hours.

Analysis of the methemoglobin in the blood (Table 10) showed that within two hours after administration, the level had risen to 35% and 51% in the two ducks. The background or natural level was 6 and 14%. At all times when blood was examined except at the time of administration, the blood of the 2,4-DNT treated ducks was chocolate-brown, or the color of root beer. The presence of the methemoglobin pigment is highly diagnostic of exposure to 2,4-DNT and other nitroaromatic compounds.

DISCUSSION

Two munition compounds were found in ERF sediments: 2,4-DNT (a nitroaromatic compound) and white phosphorus (P_4). We concluded from the extensive sampling that high explosives are not found in the water nor in surface sediments at ERF. The salt marsh immediately adjacent to the EOD area is contaminated, however, with propellants, as shown by the distribution of samples containing 2,4-DNT (Fig. 15). The source of this contamination was probably the demolition of propellants in the EOD area. The whole grains of propellant found on the EOD pad and in the adjacent salt marsh also suggest that incomplete demolition of these propellants contaminated both the EOD pad and the adjacent salt marsh. When these grains were extracted and analyzed by GCMS, the compounds found in the grain extract were identical with those found in the soil sediment extract. This spatial variability in the concentration of 2,4-DNT within a frozen bulk sediment sample also indicates that the contamination is particulate in nature as opposed to a plume coming from a point source.

Although 2,4-DNT was found locally in the salt marsh up to 50 m from the edge of the EOD, several lines of evidence suggest that 2,4-DNT is not the cause of waterfowl mortality in ERF:

- The behavior of ducks dosed with 2,4-DNT in the laboratory was not consistent with that of sick wild ducks in ERF.
- 2,4-DNT has a relatively high acute dosage (1000 mg/kg of body weight). The highest concentration of 2,4-DNT found in ERF sediment was about 60 µg/g. For a duck to consume a lethal dose, 17 kg of sediment would have to be processed.
- Methemoglobin, as indicated by blood color, was not visually obvious in any of the ducks autopsied in the field.
- The area where 2,4-DNT was found is mostly tall sedge marsh with few ponds suitable for waterfowl habitat.

Table 11. Chemical and physical properties of white phosphorus.

Property	*Value*		*Source*
Solubility in water (15°C)	2.4 mg/L		Yon et al. (1983)
Solubility in olive oil	12.5 g/L		Yon et al. (1983)
Density	1.8 g/cm^3		U.S. Dept. of Health and Human Services (1978)
Octanol–water partition coefficient	1200		Spanggord et al. (1985)
Melting point	44°C		U.S. Dept. of Health and Human Services (1978)
Autoignition temperature	30°C		Yon et al. (1983)
Vapor pressure	0.026 mm Hg at 20°C		U.S. Dept. of Health and Human Services (1978)
Oxidation states			
(Fully oxidized)	+5	P_4O_{10} (solid)*	Emsley (1989)
	+3	P_4O_6 †	Emsley (1989)
	0	P_4	Emsley (1989)
	−2	P_2H_4	Emsley (1989)
(Fully reduced)	−3	PH_3 (gas)	Emsley (1989)

*Forms H_3PO_4, $H_2PO_4^-$, HPO_4^{2-} or PO_4^{3-} in water, depending on pH.
† Forms H_3PO_3, $H_2PO_3^-$ or HPO_3^{2-} in water, depending on pH.

Evidence that support white phosphorus as a more likely cause of waterfowl mortality in ERF includes:

- White phosphorus was found in the tissues of all ducks and swans analyzed from ERF but in none of the five ducks from Susitna Flats.
- White phosphorus was found at similar concentrations in the tissues of laboratory ducks dosed with white phosphorus.
- The behavior of poisoned ducks at ERF was consistent with the behavior of ducks treated in the laboratory with white phosphorus and the behavior reported in the literature (Coburn et al. 1950). In all three instances, ducks showed lethargy, increased thirst, head-rolling (held back and swaying), violent convulsions and death.
- Lethal doses of white phosphorus are a few milligrams per duck whereas lethal doses of 2,4 DNT are in the range of hundreds of milligrams per duck.
- White phosphorus was found in the bottom sediments of shallow ponds used extensively by waterfowl.

The above comparison of experimental and field studies with white phosphorus and 2,4-DNT clearly supports the hypothesis that white phosphorus is the cause of the waterfowl mortality.

The mechanism by which white phosphorus causes sickness and death of ducks in ERF has not been published in the literature. The absence of white phosphorus in the brain tissue of the wild ducks from ERF suggest that it does not act on the central nervous system, though a product of phosphorus metabolism might be responsible. In both laboratory and field ducks, white phosphorus was found in the body fat. This would be expected of a compound like white phosphorus, which has a high affinity for oil and a high octanol–water partition coefficient (Table 11). The immediate cause of death as observed in ERF, appears to be convulsions, drowning by entanglement in vegetation or by gull or eagle predation.

The mechanism by which white phosphorus entered and was stored in ERF sediments depends upon the physical and chemical properties of white phosphorus (Table 7) as well as the water and sediment conditions in ERF. White phosphorus is a highly reactive compound, and when exposed to the atmosphere it ignites (at 30°C) and forms a liquid because of the low melting point. When a smoke projectile bursts, particles of white phosphorus ignite. Due to its high burning temperature and low melting point, white phosphorus melts, forming burning globules. When these globules hit the water (or snow or ice) surface of ERF, they would be extinguished (Fig. 22).

Because white phosphorus has a high density and a low water solubility, particles would sink through the water column into the sediments. Once an unburned white phosphorus particle settles to the bottom of a shallow pond, sedimentation would cover the particle and be preserved in the anaerobic conditions typical of salt marsh soils. In ERF, flooding of waterfowl ponds with silt-laden water from Eagle River was frequent. Redox potentials measured in the ERF sediments in which white phosphorus was found were less than −200 mV. Once buried in anaerobic sediments, oxidation will be extremely slow (Bentley et al. 1979, Sullivan et al. 1979, Davidson et al. 1987). Reduction may occur, with the generation of the highly toxic gas phosphine (Table 11) in reducing–alkaline conditions.

While assessing the environmental fate of white phosphorus, Spanggord et al. (1985) modeled the lifetime (the time required for white phosphorus to be completely oxidized) using variables such as depth of burial, radius of particle and diffusivity of oxygen through soil and

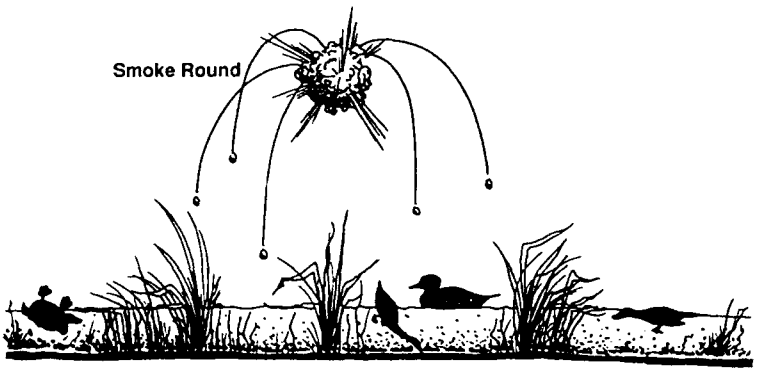


Figure 22. Proposed method by which white phosphorus from a smoke round exploding above the surface of shallow pond might be deposited and buried in Eagle River Flats sediments.

through a coat. Their model predicts that the lifetime of a 1-cm-diameter chunk buried 15 cm in an upland (not wet) soil would vary from 10 to 10,000 years, depending on whether a solid oxidized layer forms around the particle, which limits oxygen diffusion.

Two documented cases suggest that white phosphorus is persistent in aquatic environments. In 1968 a white phosphorus production facility began operating in Long Harbour, Placentia Bay, Newfoundland. Within two days of the first release into the harbor of plant effluent containing dissolved and suspended white phosphorus, dead cod, eels, flounder, crabs and lobsters were found. Mass mortality of herring occurred in subsequent months. Following the fish kills, an extensive cleanup operation was implemented in which most of the contaminated sediments were removed by dredging (Idler 1969) after the plant was closed. Sampling of areas where the sediment was not mechanically removed revealed that the concentrations of white phosphorus did not decrease significantly over an 18-month period. In the early 1970s at Pine Bluff Arsenal, Arkansas, effluent (phossy water, a colloidal suspension of white phosphorus in water) from the manufacture of white phosphorus munitions was discharged into a settling pond. After heavy rains had resuspended the settled white phosphorus and washed it into a neighboring lake, extensive fish kills were observed in the lake (Sullivan et al. 1979). These cases are evidence for the extreme toxicity of white phosphorus and its persistence in aquatic sediments.

Based on the above information and our ERF measurements of low redox potentials, high tidal flooding frequency, sedimentation or burial rates (not directly measured in ERF) and high proportion of waterlogged clay sediments, we surmise that white phosphorus in the sediments of ERF will be stored indefinitely and will continue to be a hazard to waterfowl even without additional inputs. However, we do not know with accuracy the distribution in the sediments (both vertical and horizontal), the particle size or the actual amounts of white phosphorus in ERF.

Results from previous investigations at ERF were inconclusive as to the cause of the waterfowl mortality, yet two observations of unusually high concentrations of total phosphorus were recorded, first in waterfowl tissue and then in ERF water and sediments. As previously discussed the U.S. Fish and Wildlife Service National Wildlife Research Center observed what they initially considered to be high levels of total phosphorus in the gastrointestinal tracts of waterfowl from ERF. Second, ESE (1990) concluded that total phosphorus sediment concentrations were elevated in area C. We were able to identify the waterfowl poison for several reasons. Because we collected many more sediment and water samples than had previous investigators, we had a better chance of locating a sample that would provide a clue to the poison, in this case a sediment sample that gave off what appeared to be smoke or a cloud of water vapor. Because of our experience with the chemistry of munitions, we recognized that the "smoke" might come from white phosphorus.

CONCLUSIONS

- Two sources of contamination, potentially toxic to waterfowl, were found in the ERF salt marsh and include 2,4-DNT (used as a propellant) and white phosphorus (used to produce smoke).
- 2,4-DNT is localized in its distribution in ERF and is found in the sediments of a tall sedge marsh adjacent to an explosive ordnance demolition site. Incomplete demolition of propellant grains on this EOD site is the probable source of this contamination.

- Field, literature and laboratory studies show that it is unlikely that 2,4 DNT is the cause of waterfowl mortality in ERF.
- Evidence presented here supports the hypothesis that white phosphorus (P_4), fired into ERF by mortars and howitzers, is the cause of waterfowl mortality in ERF.
- Even without additional inputs of white phosphorus, poisoning of waterfowl will likely continue in ERF. Water and sediment conditions in this salt marsh are conducive to long-term storage of white phosphorus in the sediments.
- The lead shot poisoning of waterfowl is a useful analog to the white phosphorus poisoning of waterfowl in ERF in terms of the physical size, sediment storage, mode of ingestion by feeding waterfowl, and food chain effects.
- The future military use of ERF needs to be evaluated in relation to the importance of the area as migratory waterfowl habitat, the fate and longevity of white phosphorus contamination, the other impacts of munition use and the importance of ERF as a training range for the 6th Infantry Division.

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APPENDIX A. CHEMICAL AND PHYSICAL PARAMETERS OF SEDIMENT SAMPLES COLLECTED IN EAGLE RIVER FLATS DURING AUGUST 1990

EAGLE RIVER FLATS, FT. RICHARDSON ALASKA
SAMPLING BASELINE AT EOD PAD, AREA C
AUGUST 9–21, 1990

	SAMPLE LOCATIONS									Results from RP–HPLC analysis				
	Baseline location	UTM			Water	Salinity	Redox	Vegetation	Veg. height	Concentration (µg/g)				
Sample #	Sta #/Dist(ft)	North	East	Elevation	depth (cm)	(ppt)	(mV)		(m)	RDX	TNT	2,4–DNT	2,6–DNT	2–Am–DNT 4–Am–DNT
1	10+00/28	6,800,996.8	355,572.5			1.9					0.122	0.142		
2	10+00/84	6,800,984.8	355,557.4		12			sedge	1.3			0.103		
3	10+00/140	6,800,972.6	355,548.4		1			sedge	1.07					
4	10+00/185	6,800,962.9	355,538.7		1		–83.1	sedge	1.07					
5	10+00/220	6,800,955.4	355,531.2	16.18	1			sedge	1.3					
6	10+00/257	6,800,947.4	355,523.2	16.66	1		–2.7	sedge	1.2					
7	10+00/290	6,800,940.3	355,516.1	16.52	1	4.3	–2.2	sedge	1					
8	10+00/325	6,800,932.7	355,508.6	16.78	1	3.6	–63.4	sedge	0.9					
9	10+00/359	6,800,925.4	355,501.2	16.83	1	3.5	11.7	sedge	0.95					
10	10+00/54	6,800,991.2	355,566.9	15.41	5	2.6	–54.2	sedge	1.5					
11	12+00/14	6,801,042.9	355,532.4	15.48	17	1.2	–73.7	sedge	1.2			0.034		
12	12+00/23	6,801,040.9	355,530.4	15.68	31	5.4	–41.4	open water	0					
13	12+00/35	6,801,038.3	355,527.9	14.51	33	2.7	–62.8	open water	0					
14	12+00/54	6,801,034.2	355,523.8	16.64	32	5.2	–22.2	*hippurus*						
15	12+00/79	6,801,028.8	355,518.4	14.60	30		–37.9	*hippurus*	0.25					
16	12+00/107	6,801,022.8	355,512.4	14.60	35	6.8	–221.8	hip–50%	0.3					
17	12+00/133	6,801,017.2	355,506.7	14.87	25	3	–63.4	hip–50	0.3					
18	12+00/160	6,801,011.4	355,500.9	14.27	29	6.3	–39.2	hip–70	0.32					
19	12+00/210	6,801,000.6	355,490.2	14.79	25	4.6	–2.2	hip–75	0.3					
20	12+00/244	6,800,993.2	355,482.9	15.37	13	6.4	–27.1	hip–40	0.3					
21	12+00/0	6,801,045.9	355,535.4	23.62	0							1.05		
22	14+00/30	6,801,082.5	355,485.8	15.35	7	1	–38.3	sedge	1.3					
23	14+00/38	6,801,090.3	355,488.8	14.50	32	3.2	–35.8	water–weed						
24	14+00/49	6,801,078.4	355,481.7	14.12	44	5.1	–73.7	water–weed						
25	14+00/59	6,801,076.2	355,479.5	14.05	46	4.4	–47.3	water–weed						
26	14+00/73	6,801,073.2	355,476.5	14.07	45	5.7	–250	water–weed						
27	14+00/88	6,801,070.0	355,473.3	14.48	36	5.9	–94.5	hip–2	0.3					
28	14+00/116	6,801,063.9	355,467.3	14.34	28	7.6	–32.8	hip–20	0.28					
29	14+00/154	6,801,055.7	355,459.1	14.62	17	6.9	–24.1	hip–70	0.25					
30	14+00/193	6,801,047.3	355,450.7	14.74	23	6.5	–275	hip–90	0.25					
31	14+00/224	6,801,040.6	355,444.0	14.42	29	6.6	–295	water–weed						
32	16+00/7	6,801,118.9	355,439.1	15.75	32		–8.3	sedge	1.2					
33	16+00/15	6,801,116.8	355,437.9	14.72	27	1.5	–160	open–water						
34	16+00/25	6,801,114.2	355,436.3	14.47	36		–240	open–water						
35	16+00/38	6,801,110.9	355,434.2	14.18	47	6.7	–34.1	open–water						
36	16+00/52	6,801,107.2	355,432.0	13.67	51	7.5	–226	open–water						
37	16+00/74	6,801,101.5	355,428.5	13.83	38			open–water						
38	16+00/97	6,801,095.5	355,424.8	14.21	28	6.8	–26.7	open–water						
39	16+00/116	6,801,090.6	355,421.0	14.38	29	4.9	–38.1	open–water						
40	16+00/143	6,801,083.6	355,417.5	14.13	34			open–water						
41	16+00/166	6,801,077.6	355,413.9	13.82	35	4.1	–125	hip–80%	0.26					
42	18+00/20	6,801,147.3	355,385.1	15.40	5			sedge	1.3					
43	18+00/29	6,801,145.0	355,383.6	14.72	20	5.3	–16.2	sedge	0.6					
44	18+00/34	6,801,143.7	355,382.9	13.86	35	5.2	–44.4	open water						
45	18+00/47	6,801,140.3	355,380.8	13.90	37		–85.8	water–weed						
46	18+00/59	6,801,137.2	355,378.9	14.57	26	6	–22.1	hip–10	0.2					
47	18+00/73	6,801,133.6	355,376.6	14.56	19	6.1	–26.1	hip–75	0.24					
48	18+00/95	6,801,127.8	355,373.2	14.12	25	7.9	49.5	hip–20	0.15					
49	18+00/117	6,801,122.1	355,369.7	14.49	17	7.5	–41.7	hip–10	0.2					
50	18+00/132	6,801,118.2	355,367.3	14.40	12	7	–173	sedge	1					
51	18+00/160	6,801,110.9	355,362.0	13.85	10	7	–134	water–weed						
Perpendicular														
52	20+00/26	6,801,177.6	355,332.1	14.80	25	5	–168	water–weed						
53	20+00/40	6,801,173.9	355,329.9	13.97	45	7	–285	open water				0.049		
54	20+00/52	6,801,170.8	355,328.0	13.99	45	8.2	–211	open water						
55	20+00/64	6,801,167.7	355,326.1	13.98	45	5	–166	water–mat						
56	20+00/85	6,801,162.2	355,322.7	14.10	40	7.6	–99	water–mat						
57	20+00/98	6,801,158.9	355,320.7	14.16	40	6.5	–220	water–mat						
58	20+00/111	6,801,155.5	355,318.6	14.37	33	6	–200	water–mat						
59	20+00/124	6,801,152.1	355,316.5	14.59	28	5.6	–244	water–mat						
60	20+00/137	6,801,148.7	355,314.5	14.34	35	6.3	–241	water–mat				0.022		
61	20+00/167	6,801,140.9	355,309.7	14.49	26	6.2	–220	water–mat						
62	20+00/187	6,801,135.7	355,306.5	14.96	18	4.5	–231	water–hip						
Continuation														
63	20+40/0	6,801,190.7	355,325.9	15.24	15	5	–172	sedge–90	1.3					
64	20+77/0	6,801,196.6	355,318.2	14.84	20	5.4	–255	sedge–25	0.5					
65	20+88/0	6,801,198.3	355,313.4	14.72	25	5.4	–237	water edge						
66	21+00/0	6,801,200.3	355,310.3	14.88	20	4.6	–168	*juncus–5*	0.65					
67	21+18/0	6,801,203.1	355,305.6	14.17	40	8	–163	water–mat						
68	21+34/0	6,801,205.7	355,301.4	14.08	40	7.8	–185	water–mat						
69	21+51/0	6,801,208.4	355,297.0	14.29	45		–270	water–mat						
70	21+66/0	6,801,210.7	355,293.1	14.35	45	7	–171	water–mat						
71	21+83/0	6,801,213.4	355,288.7	14.55	35		–156	water–mat						
72	21+97/0	6,801,215.7	355,285.0	14.83	28	6.4	–170	*juncus–10*	0.6					
73	14+80/50	6,801,088.7	355,463.5		40	2.2	–170	open water						

Sample #	SAMPLE LOCATIONS Baseline location Sta #/Dist(ft)	UTM North	UTM East	Elevation	Water depth (cm)	Salinity (ppt)	Redox (mV)	Vegetation	Veg. height (m)	Results from RP–HPLC analysis Concentration (µg/g) RDX	TNT	2,4–DNT	2,6–DNT	2–Am–DNT	4–Am–DNT
74	8+00/44	6,800,950.3	355,612.2	15.81	3	4.6	–136	sedge	1.3		0.467	0.442	0.224	0.272	0.298
75	8+00/55	6,800,947.9	355,609.8	15.59	5	2.6	–77	sedge	1.3		0.029	5.12	0.533		
76	8+00/67	6,800,945.3	355,607.2	15.26	2	4	–88	sedge	1.5			0.734	0.0795		
77	8+00/81	6,800,942.3	355,604.2	15.52	2	3.4	–104	sedge	1.3			0.199			
78	8+00/105	6,800,937.1	355,599.1	15.55	2	3.7	–169	sedge	1.3		0.089	2.54	0.367		
79	8+00/125	6,800,932.8	355,594.8	15.99	2	1.8	–178	sedge	1.3			0.05			
80	8+00/150	6,800,927.4	355,589.4	15.51	5	5.1	–223	sedge	1.3						
81	8+00/170	6,800,923.1	355,585.1	15.67	5	4.3	–222	sedge	1.3						
82	8+00/194	6,800,917.9	355,579.9	15.49	5	4.9	–206	sedge	1.2			0.163			
83	8+00/222	6,800,911.9	355,573.9	15.51	5	4.8	–213	sedge	1.2						
84	8+00/251	6,800,905.6	355,567.6	15.61	5	5.5	–219	sedge	1						
									1.2						
85	6+00/94	6,800,921.8	355,677.3	15.74	5	1.9	–195	sedge	1			7.36	0.548		
86	6+00/105	6,800,918.5	355,676.8	15.44	5	4.3	–204	sedge	1			4.33	0.236		
87	6+00/122	6,800,913.4	355,675.9	15.64	5	3.7	–182	sedge	1			0.061			
88	6+00/136	6,800,909.2	355,675.3	15.66	5	3.1	–122	sedge	1			0.045			
89	6+00/163	6,800,901.0	355,674.0	15.67	5	4.6	–176	sedge	1			0.385			
90	6+00/192	6,800,892.3	355,672.6	15.71	5	4.8	–175	sedge	1			4.02			
91	6+00/206	6,800,888.1	355,671.9	15.61	5	4.8	–198	sedge	1			0.876			
92	6+00/220	6,800,883.9	355,671.2	15.57	5	3.2	–203	sedge	0.7						
93	6+00/235	6,800,879.4	355,670.5	15.70	5	3.6	–153	sedge	0.6			0.026			
94	6+00/258	6,800,872.4	355,669.4	15.65	5		–213	sedge	0.6						
Additional															
95	10+00/32	6,800,996.0	355,570.7	14.87	10	4.1	–185	sedge	1.5		0.267	12.4			
96	10+00/42	6,800,993.8	355,568.6	15.22	20			sedge	1.3		115	0.148			
97	10+00/68	6,800,988.2	355,563.0	15.12	20	5.3	–229	sedge–5	0.9			0.028			
98	10+00/327	6,800,932.3	355,506.6	15.72		4.2	–149								
99	4+00/20	6,800,934.4	355,741.1	15.62	1	1.6	–200	sedge	1.6		0.031				
100	4+00/32	6,800,930.8	355,740.5	16.29	15	4.3	–202	sedge	0.8			0.658			
101	4+00/47	6,800,926.2	355,739.7	16.36	5	3.6	–202	sedge	1			1.84			
102	4+00/63	6,800,921.4	355,739.0	15.49	1	0.6	–79	sedge	0.8			0.537			
103	4+00/81	6,800,916.0	355,738.1	15.78	0			sedge	0.8			0.12			
104	4+00/99	6,800,910.6	355,737.2	15.62	1			sedge	0.8			0.142			
105	4+00/121	6,800,904.0	355,736.2	15.83	0			sedge	0.8			0.071			
106	4+00/139	6,800,898.6	355,735.3	15.80	0			sedge	0.9			0.659			
107	4+00/163	6,800,891.3	355,734.1	15.66	0	4.6	–67	sedge	0.5			0.475			
108	4+00/192	6,800,882.6	355,732.7	15.83	0	3.5	–143	sedge	0.6						
Old rocket															
109	7+50/90	6,800,930.3	355,632.4												
Smokehole															
110	7+54/139	6,800,915.7	355,628.8	14.75	5			sedge			0.013	2.15	0.171	0.041	0.104
111	7+54/140	6,800,915.4	355,628.7	13.10				sedge							
112	7+54/140	6,800,915.4	355,628.7	13.10				sedge							
113	7+54/140	6,800,915.4	355,628.7	13.10				sedge							
114	7+54/140	6,800,915.4	355,628.7	13.10				sedge							
Along Bank At base			y									sediment	samples		20 cm depth
115	2+00/26	6,800,922.9	355,800.9		0	1.3	–145	sedge	1			0.027			
116	2+50/20	6,800,927.1	355,786.2		1	0.7	–170	sedge	1.2			0.454			
117	3+00/20	6,800,929.5	355,771.1		1	1	–201	sedge	1.2						
118	3+50/20	6,800,932.0	355,756.1		0	2	–193	sedge	1.1		0.196	62.9	4.47	0.133	0.281
119	4+55/35	6,800,932.5	355,723.8		0	1.6	–177	sedge	1		0.0345	2.18	0.166		
120	5+00/54	6,800,929.0	355,709.3		2	1.6	–159	sedge	0.8		0.0509	0.13			
121	5+50/78	6,800,924.2	355,693.1			1.6	–133	sedge	0.6		0.0748	8.46	0.64		
122	6+50/87	6,800,926.3	355,662.6					sedge	0.6		0.1	15.4	1.1		
123	7+00/64	6,800,935.7	355,648.7				–60	sedge	0.6		0.315	84	2.36		
124	7+50/53	6,800,941.4	355,634.1			2	–62	sedge	0.5		0.039	1.54	0.39		
125	8+50/27	6,800,977.8	355,600.6		5	1.6	–145	sedge	1.2		0.147	36.6	2.51		
126	9+00/26	6,800,975.7	355,594.5			2.1	–183	sedge	1		0.0293	0.619			
Smokehole															
127	7+54/140	6,800,915.4	355,628.7												
Along Bank															
128	9+50/37	6,800,984.1	355,581.3		5	3	–180	sedge	1.2			2.78	0.216		
129	10+50/32	6,801,006.7	355,560.8		15	1.2	–176	water–sedge			0.141	24.5	1.92		
130	11+00/21	6,801,019.8	355,552.4		10	1.1	–159	sedge	0.8		0.134	0.608	0.0532		
131	11+50/16	6,801,031.7	355,542.7		5	1	–30	sedge	1		0.26	0.27		0.268	0.259
132	12+50/16	6,801,053.2	355,521.2		5	1	–129	sedge–90	0.8		0.018	0.168			
133	13+00/23	6,801,062.4	355,508.9		5	1	–232	sedge–40	0.8						
134	13+50/25	6,801,072.8	355,497.6		2	1	–192	sedge–100	1.2			0.0399			
135	14+50/19	6,801,091.9	355,476.2		10	1	–108	crater							
136	15+00/18	6,801,100.2	355,463.4		10	1.2	–170	sedge	0.8						
137	15+50/13	6,801,109.4	355,451.2		5	1.2	–67	sedge	0.8						
138	16+50/12	6,801,125.6	355,425.3		10	1.4	–240	sedge	0.8						
139	17+00/14	6,801,133.0	355,412.0		10	1.6	–211	sedge	0.8						
140	17+50/14	6,801,141.0	355,399.0		5	1.5	–208	sedge	0.8						
141	18+50/23	6,801,154.5	355,371.6		15	1	–252	sedge–50	1						
142	19+00/0	6,801,168.4	355,362.3			4.6	–186								
143	19+48/0	6,801,176.1	355,349.8			4.9	–182								
Diagonal line with blind near 150															
144	20+01/346 *	6,801,196.2	355,231.5	14.49	22	5.7	–212	water–hip							
145	20+01/374 *	6,801,197.2	355,223.0	14.43	22	4.4	–243	water–mat							
146	20+01/402 *	6,801,198.1	355,214.5	15.36	8	5	–178	water–hip							
147	20+01/443 *	6,801,199.5	355,202.1	15.59	15	5.1	–221	water–mat							
148	20+01/488 *	6,801,201.1	355,188.5	15.29	12	5	–156	open water							
149	20+01/518 *	6,801,202.1	355,179.4	15.17	15	4.8	–230	water–mat							
150	20+01/557 *	6,801,203.4	355,167.6	15.34	11	4.4	–236	open water							
151	20+01/597 *	6,801,204.8	355,155.5	15.39	11	5	–215	open water							
152	20+01/618 *	6,801,205.5	355,149.1	15.44	8	4.4	–233	open water							
153	20+01/636 *	6,801,206.1	355,143.7	15.59	1	5.7	–217	open water							
154	20+01/660 *	6,801,207.0	355,136.4	15.10	17	5.4	–192	open water							
155	20+01/705 *	6,801,208.5	355,122.8	15.24	7	7	–225	open water							
Near sample 76		(near crater)													
156	8+20/67	6,800,949.6	355,602.9			1.8	–166	sedge	1.6		0.118	52.9	4.23		

Sample #	SAMPLE LOCATIONS Baseline location Sta #/Dist(ft)	UTM North	UTM East	Elevation	Water depth (cm)	Salinity (ppt)	Redox (mV)	Vegetation	Veg. height (m)	Results from RP-HPLC analysis Concentration (µg/g) RDX	TNT	2,4-DNT	2,6-DNT	2-Am-DNT	4-Am-DNT
EOD TRENCH 1	(On pad)														
157	8+00/–20	6,800,964.1	355,626.0		30							0.465			
158	8+00/–20	6,800,964.1	355,626.0		158							*0.056*			
159	8+00/–20	6,800,964.1	355,626.0	23.03	0					0.076	0.061	0.089		0.061	0.078
160	8+00/–20	6,800,964.1	355,626.0		110					0.0515		0.065			
161	8+00/–20	6,800,964.1	355,626.0	14.27	280					0.044		0.014			
162	8+00/–20	6,800,964.1	355,626.0		10					0.0498		0.845	0.085	0.116	0.219
EOD TRENCH 2	(Pad extension)														
163	7+54/75	6,800,935.0	355,631.9	14.09	100										
164	7+54/75	6,800,935.0	355,631.9		80						0.027				
165	7+54/75	6,800,935.0	355,631.9		20						0.128	0.221		0.71	0.936
166	7+54/75	6,800,935.0	355,631.9		50										
167	7+54/75	6,800,935.0	355,631.9		100										
168	7+54/75	6,800,935.0	355,631.9		70						0.104				
169	7+54/75	6,800,935.0	355,631.9	17.21	0						0.194	53.9	3.43	0.731	0.74
Near Sample 96		(4' either side)													
170	10+00/46	6,800,992.9	355,568.6			1.6	–155					0.043			
171	9+96/42	6,800,992.9	355,570.3			1.6	–148				0.07	3.27	0.244	0.029	0.068
172	10+04/42	6,800,994.6	355,568.6			1.6	–158				0.038	0.45	0.135		
Stake marking maximum water level at high tide on 5/25/90															
	7+53/72			18.64											

* Sampling line is actually located along a line at a 155° angle from the baseline (or 25° from the reverse azimuth), starting from Sta. 20+00. The 20+01 designation is used to differentiate it from the previously sampled right angle line at 20+00.

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13. ABSTRACT (*Maximum 200 words*)

The death of hundreds of migrating dabbling ducks and 10–50 swans has been documented annually for the last ten years in Eagle River Flats (ERF), an estuarine salt marsh on Ft. Richardson, Alaska. This marsh has been used for the past 40 years as an artillery impact range by the U.S. Army. During May and August 1990, CRREL collected 250 sediment and water samples and analyzed them for munitions residues. We found 2,4-DNT in a limited area of Eagle River Flats not used by waterfowl and white phosporus in sediments from the bottom of shallow ponds where waterfowl feed. Tissues from waterfowl observed to die or found dead in the salt marsh were collected, and we found white phosphorus in the gizzards of all 11 carcasses collected in Eagle River Flats. Adult mallards dosed in the laboratory with white phosphorus showed identical behavioral symptoms to those of wild ducks observed to become sick and die in Eagle River Flats. All evidence indicates that white phosphorus, as a particulate in the sediments, is responsible for the death of waterfowl in Eagle River Flats. Since the bottom sediments of the shallow salt marsh ponds are anaerobic, the white phosphorus particles will persist in the sediments indefinitely and remain a threat to waterfowl.

14. SUBJECT TERMS

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